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HYDROCARBON PROCESSING®

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Cover Image: View of the 425,000-bpd CITGO refinery in Lake Charles, Louisiana (U.S.). Photo courtesy of CITGO Petroleum Corp.





Industry Perspectives

Hydrocarbon Processing's Publisher recognized as 2021 Top Women in Media honoree



Hydrocarbon Processing would like to congratulate Catherine Watkins, Vice President Downstream and Publisher, *Hydrocarbon Processing*, *Gas Processing & LNG* and *H2Tech*, for being honored as one of the top women in media for 2021.

The Top Women in Media Awards are presented by AdMonsters and Folio to honor women who are making a significant impact in the publishing industry. Ms. Watkins was recognized in the category of "Entrepreneurs" as someone who has launched or rebuilt brands and continues to work tirelessly towards their success.

Ms. Watkins joined Gulf Energy Information in Houston, Texas as Publisher of *Hydrocarbon Processing* and *Gas Processing & LNG* 5 yr ago, after working as a successful Sales Manager in Europe and the Middle East. She took on the role of Publisher with a solid understanding of advertisers' needs and balances it with her deep respect for editorial integrity.

She believes that communication and collaboration are critical to success and has maintained and grown strong relationships throughout the male-dominated refining and petrochemical industry. She has forged partnerships and developed collaborative relationships with many stakeholder organizations to increase circulation and visibility with professionals at various stages of their careers, from entry-level engineers to CEOs of some of the largest companies in the world.

This connection with the industry has allowed her to quickly launch successful new products. Last year, she recognized the need for a publication to serve the hydrogen community, a rapidly growing segment of the clean energy sector. She and her team quickly responded by launching *H2Tech*, along with a biweekly newsletter, podcast and technical conference, all within the span of a few months. This drive to create an informative, well-respected publication to help move the world's energy needs to a more sustainable path has already garnered significant praise from industry leaders around the world.

The honorees were celebrated at a luncheon on December 1 at the Edison Ballroom in New York City. **HP**

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Past, present and future: *Hydrocarbon Processing* celebrates 100 yr of publishing

It is my esteemed honor to announce that *Hydrocarbon Processing* is entering its centennial year of publishing. Over the past 100 yr, the publication has focused on the latest technologies and innovations that have advanced the hydrocarbon processing industry. This includes the earliest processes for thermal cracking to the numerous complex processes for refined and petrochemical products production and the advancement in digital technologies to optimize plant operations.

First published in 1922, *Hydrocarbon Processing* has evolved over the many decades in alignment with advancements in processing technologies. At its inception, the publication was called *The Refiner and Natural Gasoline Manufacturer*, taking several names—*Refiner* (1924–1952), *Petroleum Refiner* (1953–1963), *Hydrocarbon Processing and Petroleum Refiner* (1963–1966)—until establishing the name *Hydrocarbon Processing* in 1966.

With the start of the publication's centennial year, the editors of *Hydrocarbon Processing* will be providing our global readers with several new sections of the magazine, including a detailed history of the hydrocarbon processing industry.

History of the HPI series. In this issue, the editors detail the history of the hydrocarbon processing industry up to the 1930s. This overview provides a rich history of the industry's origins and how the discovery of kerosene changed the course of history and ignited a new era in refined products demand. The analysis also examines the beginning of the modern petrochemicals industry and several technology breakthroughs. The History of the HPI series will continue through the September issue, with each issue detailing a specific decade in the history of the refining and petrochemicals industries, as well as the people that helped shape the course of the HPI.

Industry Pioneers. In addition, *Hydrocarbon Processing*'s Industry Pioneers series will celebrate the accomplishments of those that have made extraordinary differences within the industry and have contributed to the advancement of refining and petrochemicals production. The scientific advancements in processing technologies have provided people around the world with a higher standard of living, modern conveniences, life-saving equipment and much more.

HP Flashback. This section will showcase some of the major technical articles that have been published within *Hydrocarbon Processing*. Each issue, the editors will provide the titles, technologies and summaries of technical articles published in various decades of the publication. In this issue, dozens of articles are listed that were published from 1922–1930. *HP Flashback* will not only provide an interesting look back at major technical trends in various decades, but will also show how the industry has advanced over the past 100 yr.

New sections. *Hydrocarbon Processing* has continuously evolved with the major trends and technologies shaping the refining and petrochemicals industries. The publication continues to do so, especially during the industry's energy transition. This year, the editors have included several new topics, including biofuels, alternative/renewable fuels, plastics recycling, biomass/co-processing, plant turnarounds, refining and petrochemicals integration, carbon capture/CO₂ mitigation, green petrochemicals, the green refinery, the circular economy and digital transformation, among others.

With the new sections of the magazine and the focus on the last 100 yr of technological advancements, the centennial year of *Hydrocarbon Processing* is sure to be one to remember. **HP**

INSIDE THIS ISSUE

8 **HP Construction.** This month's Business Trends section details major capital project construction contract awards around the world.

16 **Sustainability.** Many companies are optimizing operations for greater safety, reliability, efficiency and environmental and social awareness. This month's Special Focus section details major trends in sustainability initiatives globally.

33 **Biofuels, Alternative/Renewable Fuels.**

This section examines key considerations for the design and operation of a renewable diesel plant, as well as comparing green fuels for marine engines.

46 **History of the HPI.**

This month, the editors provide the origins of the modern refining and petrochemicals industries up to the 1930s, early industry pioneers, and a mixture of technical articles, columns and headlines published in the 1920s by the forerunner of *Hydrocarbon Processing*, *The Refiner and Natural Gasoline Manufacturer*.

63 **Bio-based Processing.**

Refineries are looking for ways to easily incorporate biofeedstocks into their existing infrastructure. This article describes the impacts on a refinery's existing amine system, sour water stripper and sulfur recovery unit, as well as some operational and design options available to manage those impacts.

71 **Heat Transfer.** This article

details several routes to show that revamping a fired heater can both reduce emissions and improve the bottom line.

AFRICA

Eni plans to launch its 3.4-MMtpy FLNG vessel offshore Mozambique this year. The *Coral Sul* FLNG vessel is being built by **Samsung Heavy Industries**. The vessel will utilize **Air Product's** dual mixed-refrigerant process.

BP announced it will take a final investment decision (FID) on Phase 2 of the Greater Tortue Ahmeyim LNG project in late 2022/early 2023. The project involves the development of offshore natural gas fields between Mauritania and Senegal. Phase 1, with a total processing capacity of 2.5 MMtpy, is underway, with completion scheduled for late 2023. If greenlighted, Phase 2 will double the facility's capacity to 5 MMtpy.

ASIA-PACIFIC

Lianyungang Petrochemical Co. Ltd. awarded **LyondellBasell** a technology licensing contract for a new 400,000-tpy high-density polyethylene (HDPE) plant. The new unit, which will utilize LyondellBasell's Hostalen Advanced Cascade Process, will be built in Lianyungang, Jiangsu Province, China.

Cosmos Oil and **JGC Holdings** plan to build Japan's first sustainable aviation fuel (SAF) production plant. The project will utilize Honeywell Ecofining technology to convert used cooking oil into renewable jet fuel. The Econfining process was developed by **Honeywell UOP** and **Eni** that converts non-edible natural oils, animal fats and other waste feedstocks to Honeywell Green Diesel and Honeywell Green Jet Fuel, which are chemically identical to petroleum-based counterparts. The new SAF plant is scheduled to begin operations in 2025.

Thirumalai Chemicals Ltd. greenlighted the development of a new plant to produce phthalic anhydride and fine chemicals. The 90,000-tpy plant will be in Dahej, Gujarat, India. The facility is

expected to begin operations in 2H 2024.

Numaligarh Refinery Ltd. (NRL) has let another contract for the expansion of its 6-MMtpy refinery in Brahmaputra, India. NRL awarded **thyssenkrupp Industrial Solutions Pvt. Ltd.** an engineering, procurement, construction and commissioning (EPCC) contract for a new 6-MMtpy combined crude vacuum distillation unit and amine treating unit. This award is on top of the work thyssenkrupp Industrial Solutions is already conducting on the expansion project—the company was awarded an EPC and management (EPCM) contract for several units being built (a petrochemical fluidized catalytic cracker, an LPG treatment unit, a naphtha hydrotreating unit and isomerization units, among others).

NRL is investing nearly \$3.6 B to expand its refinery by 3 MMtpy to 9 MMtpy. The project, scheduled to be completed by 2024, includes the revamp of the refinery's delayed coking unit to increase capacity.

Jiangsu Sailboat Petrochemicals Co. is working with **Carbon Recycling International** on a carbon recycling plant. The Jiangsu Sailboat Green Methanol plant—to be in Lianyungang, Jiangsu province, China—will recycle approximately 150,000 tpy of carbon dioxide (CO₂) and 20,000 tpy of hydrogen to produce 100,000 tpy of methanol. The \$35-MM project is scheduled to go online in 2023.

KBR will license technology to a new dual-pressure nitric acid plant in South Korea. The 1,200-tpd plant is being developed by **Hanwha** at its operations in Yeosu. According to KBR's press release, the company will provide licensing, basic engineering design and technical support.

ExxonMobil has greenlighted a \$10-B petrochemical complex to be developed in Huizhou City, Guangdong province, China. The Dayawan plant will include a 1.6-MMtpy flexible steam cracker that will

feed downstream units, including three PE lines and two polypropylene (PP) lines.

Chennai Petroleum Corp. Ltd. awarded consultancy and engineering and construction contracts to **McDermott** for the company's 9-MMtpy grassroots Cauvery Basin refinery. McDermott will handle the project management consultancy and EPCM work on the project, which includes the construction of more than dozen units.

GAIL Ltd. is building India's first propane dehydrogenation (PDH)-PP plant. The \$1.2-B facility will use propane to fuel the PDH unit to produce propylene. The propylene feedstock will be processed into 500,000 tpy of PP. **Engineers India Ltd.** was awarded the EPCM contract on the project, which will use the CATOFIN process technology from **Lummus Technology** and proprietary catalysts from **Clariant**. The PDH-PP plant will be in the Usar Industrial Area, Usar, Maharashtra, India. Operations are scheduled to begin in 2024.

GAIL is also expanding PP capacity at its existing PP unit in Pata, Uttar Pradesh, India. The PP expansion project will enable the facility to increase PP production by 60,000 tpy. Engineers India Ltd. will oversee the EPCM contract, while **W. R. Grace** is the technology licensor for the plant.

Triangle Energy has awarded a contract to **Plant Process Group** to conduct front-end engineering design (FEED) work on a refinery project in Western Australia. Triangle Energy plans to build a 5,000-bpd flexible feed renewable fuel refinery in the North Perth basin in Western Australia. FEED work is expected to be completed by the end of 1Q 2022, with full operations scheduled to begin in 1Q 2024.

CANADA

Northern Petrochemical Corp. plans to build a carbon-neutral ammo-

nia and methanol production facility in Alberta, Canada. The \$2.5-B project will use natural gas to produce 200 tpy of blue ammonia and blue methanol, which will be exported to demand centers primarily in Asia. The capital-intensive project, which took advantage of Alberta's Petrochemicals Incentive Program, is scheduled to begin operations in 2026.

Oxy Low Carbon Ventures and **Squamish Huron Clean Energy Corp.** have awarded a contract to **Worley** to conduct early FEED on an air capture-to-fuels facility. To be built in British Columbia, the facility will use **Carbon Engineering's** Direct Air Capture and AIR TO FUELS technologies to capture CO₂ from the atmosphere and convert it into ultra-low carbon fuel. Construction is scheduled to begin in 2023. Once operations commence in 2026, the plant will produce up to 100 MMl/yr of fuel.

Arbios, a JV between **Canfor** and **Licella Holdings Ltd.**, plans to build a plant that will convert sawmill residues

into biofuels. The project is being developed at Canfor's Intercontinental Pulp Mill site in Prince George, British Columbia. The plant will convert 25,000 t of wood residue into more than 50,000 t of biocrude, which can be further processed into low-carbon transportation fuels. The Arbios plant is scheduled to begin operations in 1H 2023.

LATIN AMERICA

In early November 2021, **Sempra Energy** announced plans to build a second LNG export terminal on the Pacific Coast. The Vista Pacifico LNG terminal will be in Topolobampo, Mexico, on the Gulf of California. The 3 MMtpy–4 MMtpy terminal will receive natural gas feedstock from the Permian shale basin in Texas (U.S.).

MIDDLE EAST

Abu Dhabi National Oil Co. (ADNOC) and **ADQ** signed a partnership agreement with **Mitsui & Co.** and **GS Energy Corp.** to develop the U.A.E.'s first

blue ammonia project. The project, which will produce ammonia from nitrogen and clean hydrogen derived from natural gas feedstocks, will be in the TA'ZIZ Industrial Chemicals Zone in Ruwais.

ADNOC also signed an agreement with **Borealis AG** to develop the Borouge 4 project in Ruwais. The \$6.2-B project will expand the existing Borouge complex by adding a fourth ethane cracker and downstream facilities. The 1.5-MMtpy ethane cracker will provide feedstock to two 700,000-tpy PE plants. The project also includes a hexene-1 unit and carbon capture. Once completed in 2025, Borouge will become the world's largest single-site polyolefin complex.

U.S.

Renewable Energy Group awarded an EPCM contract to **Wood Group** for its renewable fuels expansion and improvement project. The \$950-MM project—located in Geismar, Louisiana—will expand the facility's capacity by 250 MMgpy. Mechanical completion is scheduled to be completed by 2023, with full operations beginning in 2024.

Cerilon GTL plans to invest more than \$5.1 B to build two gas-to-liquids (GTL) plants. The company is developing a \$2.8-B GTL plant in Trenton, North Dakota. The facility will use domestically-sourced natural gas to produce 24,000 bpd of ultra-low-sulfur diesel, along with Group 3 base oils, jet fuel and naphtha. Phase 1 development is scheduled to begin in early 2023. The company is also developing a similar facility in El Reno, Oklahoma. The \$2.35-B plant will use natural gas to produce ultra-low-carbon fuels.

In Garner, Iowa, **Greenfield Nitrogen** is building the first green ammonia plant in the U.S. Midwest. The 240-tpd facility will use renewable feedstock to produce green ammonia for domestic use. Greenfield Nitrogen is working with **NextChem**, **MET Development** and **Stamicarbon**, subsidiaries of **Maire Tecnimont**, to develop the project. NextChem will prepare the feasibility study, MET Development will assist Greenfield Nitrogen on the development of the project and Stamicarbon will provide its STAMI Green Ammonia technology to the plant. **HP**

Try solving—instead of managing—equipment problems

Good managers manage people who solve problems. Average managers keep problems in check—i.e., they “manage” problems but often allow these problems to persist. An actual example involving mixers will drive home the point.

Blaming the wrong part. It is not unusual for mechanical seals in mixers to get blamed for failures that were preceded by lubrication-induced bearing distress. Such was the case for years on about a dozen large 200-rpm/160°F mixers with massive rolling element bearings costing well over \$12,000 each. The owner company had an anti-oil mist bias for reasons that defied logic and disregarded the fact-based experience of its leading competitors. Chances are the company allowed itself to be influenced by strong personalities assigned to the maintenance department. Strong personalities have been known to trust “gut feelings,” anecdotes and mere intuition. Their faith in these often takes precedence over science and solid experience.

There is merit in managing facts. Several facts were brought to the attention of the owner company in the hope that newly hired engineers would listen to experience-based truths. Concentrating on applicable science was advocated by an expert when a clueless facilitator reached out to him. The expert advised against throwing more money at repeat problems that others had solved 40 yr ago. Much earlier, the expert had hoped for an opportunity to tell site managers that every type and style of rolling element bearing can be lubricated with pure oil mist. He would have explained why the since-retired storyteller’s anecdotes were leading the company away from the solution and deserved to be disregarded. *Eliminating* repeat problems is always better than wasting resources by *managing* repeat problems.

The expert showed that well-designed, small, fully closed (recirculating) liq-

uid oil spray modules and atomized oil mist modules exist today. Either type of \$6,000 module being filled with a gallon of ISO VG 100 (~90% PAO and ~10% dibasic ester) synthetic lubricant would have solved the problem a long time ago. Again, it goes without saying that managing true problem-solvers adds permanent value, whereas managing problems that continue to drag on can do serious damage to a commercial entity.

When asked to first discuss grease-related matters, the expert made the following points:

- Lube optimization at the prevailing temperatures does not favor costly PFPE-PTFE greases. Other properly applied greases will also work.
- No type or style of greased bearing will live long when grease reaches only some, but not all, of its rolling elements.
- Successful use of PFPE-PTFE greases at this site would require fully sealed bearings.
- Sealed bearings with PFPE-PTFE fill have an anticipated life of 10 yr.
- Non-shielded (open) bearings with properly applied shear-stable premium electric motor (EM) synthetic greases would survive, if (properly) regreased every 6 mos.
- Timed, pressurized grease injection is possible, as is directed (aimed) pure oil mist application with rifle-bored classifiers designed for slow speed bearings.
- The best available bearing protector seals should be used. Best available implies using styles with diagonally-moving O-rings contacting generously sized contoured-surfaces.
- Liquid oil pumparound (recirculating oil) modules of the standard type and style used for pressurized dual mechanical seals would also solve the problem.
- Experience captured elsewhere would be helpful in any comparison.

We will never know which option was ultimately implemented by the owners of this problem. However, it is fair to assume that reading one or two recently published books and implementing any of these time-tested options would have saved the owners millions of dollars.

Grooming motivated learners. There is an important lesson to be learned here: problem solvers start out as motivated learners who become value-adders by reading and absorbing fact-based books. They should be expected to attend well-focused and wholly experience-based training sessions, thereby acquiring knowledge and becoming professionals who rely on fact-based science. Acting on a “gut feeling” and then wasting time on unproductive experimentation has no place in situations where the achievements of the competition can be summarized as consistently safe and reliable run-length extension.

Hopefully, the mixers’ owners will get to the point where its managing personnel, irrespective of actual job function, add value by solving problems instead of merely managing problems. To the extent outside facilitators are asked to assist in root cause analysis, a common-sense approach would be to enlist facilitators who possess first-hand knowledge of bearings and optimized lubrication. Choosing one’s facilitator wisely would accelerate arriving at fact-based solutions. **HP**



HEINZ P. BLOCH resides in Montgomery, Texas. His professional career commenced in 1962 and included long-term assignments as Exxon Chemical's Regional Machinery Specialist for the U.S. He has authored or co-written more than 780 publications, among them 24 comprehensive books on practical machinery management, failure analysis, failure avoidance, compressors, steam turbines, pumps, oil mist lubrication and the just released, “Optimized Equipment Lubrication,” (DeGruyter, Berlin/Germany, ISBN 978-3-11-074934-2). Mr. Bloch holds BS and MS degrees (cum laude) in mechanical engineering. He is an ASME Life Fellow and was awarded life-time registration as a Professional Engineer in New Jersey.

Decarbonizing ethylene production



STAN KNEZ is the Chief Technology Officer for Technip Energies and is part of the Executive Committee. In this role, Mr. Knez manages the company's technology portfolio, leads the innovation and R&D programs and oversees the company's product lines. He has more than 25 yr of industry experience in the global upstream and downstream industry, strongly focused on technology portfolios and alliances.

Previously, Mr. Knez was Senior Vice President of Process Technology for Technip Energies and its predecessor, TechnipFMC, President of Technip Stone & Webster Process Technology, and Executive Vice President of Technology for Shaw Energy & Chemicals Group. He also served as Vice President of Downstream Operations for KBR Energy and Chemicals.

Mr. Knez earned an MS degree in chemical engineering from Cleveland State University and an MBA in finance and international business from the University of St. Thomas. He earned his Bch degree in chemical engineering from Case Western Reserve University.

Hydrocarbon Processing (HP) sat down with Stan Knez (**SK**), Chief Technology Officer, Technip Energies, to get his insights on decarbonization, digital and process technologies and sustainability within the processing industries.

HP: At present, what are some of the main topics your clients are focused on?

SK: We see a concerted focus on energy transition. Companies are looking to implement their sustainability strategies

and ESG mandates, as well as anticipating how to meet current and future low carbon requirements. Today customers are asking us, "What are the pathways to low and zero carbon?" Of course, the main themes are CO₂ reduction and the use of recycled feedstocks.

HP: In terms of decarbonizing ethylene production, where is that current technology?

SK: First, we want to reiterate that energy efficiency remains the starting point of energy reduction and decarbonization, so there are still ways for us to improve energy efficiency and hence lower emissions. Recently, we designed a low-carbon furnace that can mitigate up to 30% of CO₂ emissions.

We have also developed an ethylene decarbonization roadmap, which outlines the pathways that will allow the ethylene industry to move to net-zero. Key facets of that roadmap include:

- The use of hydrogen as a fuel
- CO₂ capture
- Emissions reduction (e.g., low-carbon furnace)
- Electrification.

The main issues with these solutions are the economics and having a route to store or use the CO₂.

HP: Regarding carbon capture, there has been a significant uptick in news about CO₂ capture over the past year. In your opinion, is CO₂ capture available today?

SK: The technology to capture CO₂ from post-combustion streams is available today. Of course, we have been capturing CO₂ from process streams for a long time across many industries, but post-combustion streams are the ones that are, of course, very important to decarbonize many industries, so that technology has been proven at industrial scale, mainly in the power sector.

Technip Energies can offer carbon cap-

ture technology to be applied to new and existing crackers. I would say the challenge is to continue to innovate and improve on the CAPEX (capital expenditures) and OPEX (operating expenditures).

The other thing we must think about regarding carbon capture applications is what to do with the CO₂ once it is captured.

HP: Regarding the ethylene decarbonization roadmap, two of the specific items you mentioned were electrification and hydrogen. What role do you see electrification playing in the future of ethylene production?

SK: It has a significant role to play. However, the extent to which it will be utilized to reduce, for example, ethylene plant CO₂ emissions depends very much on the continued reduction of the carbon footprint associated with electricity generation. The cost and availability of large quantities of low-carbon electricity from renewable sources is needed. Then, we must develop new technologies—such as electrically heated furnaces—that can then deploy this electrification in chemical plants.

In an ethylene plant, the steam cracking furnace utilizes hydrocarbon fuel to provide the endothermic heat required for the cracking reaction. We have designed a proprietary furnace that can electrify the cracking operation. This approach avoids CO₂ emissions from the cracking furnaces. In addition, we can take advantage of low-carbon electricity using electric motor drives instead of steam turbine drives on the main compressors.

HP: Where do you see hydrogen playing a role in ethylene production?

SK: Hydrogen has significant potential for energy generation on a global basis, as hydrogen burns without generating CO₂. We are looking at displacing fresh hydrocarbon fuels with hydrogen. For example, at our Rotterdam test facility, we success-

fully demonstrated 100% hydrogen firing, with minimized NO_x (nitric oxide). This opens the opportunity to move to commercial application in an ethylene cracker.

HP: What are some future technologies that you see being developed to decarbonize the hydrocarbon processing industries?

SK: The industry is developing many alternative technologies for the decarbonization of the ethylene process. These are principally focused on reducing CO₂ emissions from the furnaces, which is the main source of carbon emissions in a steam cracker. For example, in addition to the electric furnace, we are also developing—in partnership with Siemens Energy—turbomachinery that cracks feed using shockwave technology. Innovation will drive new technologies and new approaches to lower carbon emissions.

We are also looking at another pathway that involves reacting captured CO₂ from plants with hydrogen to produce green hydrogen to make Hummingbird® ethanol. We then could utilize our

Hummingbird® ethanol-to-ethylene technology to produce green ethylene.

HP: In the next 20 yr–30 yr, will steam cracking play a role in ethylene manufacturing?

SK: 2050 sounds like a long way away, but it is only 30 yr, so we have a lot to do to get where we need to go. The vast majority of the world's olefins today are manufactured by the steam cracking process and there really are no current low-carbon commercialized alternatives at a similar scale that could replace steam cracking.

At Technip Energies, we see the main challenge to the industry to be the production of olefins by steam cracking but with much lower CO₂ emissions. When we look at 2050, we expect that ethylene production will be significantly decarbonized, and circularity will play an integral role in the process.

HP: Can you provide your thoughts on the circular economy?

SK: Yes, circularity is on the minds of many in the industry. It is a strategic intent

for the ethylene industry. We have been busy developing solutions that can address our clients' needs to, for example, introduce a level of circularity into their crackers. We can provide a complete pyrolysis and purification solution that will allow recycled plastic waste to be fed to the cracker, replacing the fresh hydrocarbon feed.

From the cracker side, we have been studying the effect of recycled feed as it is being introduced to the cracker in terms of performance and reliability. That is a very important question that our ethylene clients are asking us. We are also studying the potential of feeding biomass to the cracking furnace. We see many different approaches that could become technical and economic avenues to support the decarbonization of the industry.

Want more? You can listen to the full discussion with Stan Knez on decarbonizing the ethylene industry by listening to “Decarbonizing ethylene production and the HPI’s energy transition” on The Main Column podcast page on HydrocarbonProcessing.com. **HP**



Atlas

Be cautious with systems that are not foolproof

Mechanical systems, especially rotary equipment, are designed to support easy maintenance jobs with less complexity and low chances of incorrect installation. However, due to design constraints, systems are not completely foolproof, so there are chances of errors during maintenance.

These errors could be a result of a lack of experience or negligence. Examples of these errors include:

- **Angular contact bearings installed in pairs (face-to-face and back-to-back arrangements):**

This error is more related to a lack of understanding of bearing arrangements and the pros and cons of both types.

- **Replacement of coupling bolts with non-matched ones:**

This type of error is related to poor maintenance practices. Coupling balances require a complete assembly, so each fastener plays a significant role in coupling. The replacement of any bolt with an alternate of

lower or heavier mass can cause balance problems.

- **Rotary component on a double key:** Installation of rotary components should be a priority. Components on two keys, on two grub screws or taper bore arrangements should always be replaced as per punch markings or temporary markings to maintain rotor balance.

A similar problem in a two-stage centrifugal pump is discussed here. The following are the specifics on the pump:

- Name: UGA-121B
- Type: Two-stage centrifugal pump
- Bearing support: Simply supported [NU211 at the drive-end (DE) side and 2 x 7309 at the non-drive end (NDE) side]
- Service: Process condensate
- KW rating: 132 kW.

Observation. The UGA-121B process condensate pump in a urea plant was under a scheduled routine of condition monitoring. It was running stable with maximum vibrations of 4.5 mm/sec rms and no abnormality was noticed. After monitoring it for about 45 d, the operator observed a gradual increase in vibrations and enveloped acceleration values. The noise was increasing as well, and the same was monitored during a routine data collection. Spectrum analysis concluded the bearing fault ball pass frequency inner (BPFI) of the thrust bearing was the problem.

Vibration continued to increase, so a bearing replacement was planned on the pump. Upon inspection, bearings were found to be damaged and removed (FIG.1). Spalling was observed on one of the angular contact bearings, while the other had normal running marks. This may be due to unidirectional force and degradation of oil quality. During the monitoring period of 45 d, a slight increase in bearing housing temperature was observed, peaking to 60°C. This increase in temperature

changed the oil color to slightly blackish. Only after heating can the angular contact bearing with spalling marks be removed, and this bearing removal caused some marks on the bearing seating area.

Assembly. Before starting the pump assembly, it was decided to replace the shaft and bearings due to some markings near the impeller hub area. Assembly was completed with a new shaft, new bearings, an old sleeve and old impellers. The pump was put in place, coupled, aligned and started for trial. Vibration data was collected and, surprisingly, the horizontal vibrations on both the DE and NDE were observed to be remarkably high (around 20 mm/sec rms).

A dominant peak running speed of 1X rpm and 18 mm/sec rms amplitude were noticed in the spectrum. Further analysis was done using the phase data collection. Phase data showed a 90° phase shift between the vertical and horizontal position of the DE side bearing and NDE side bearing. Phase measurements at the horizontal direction of the DE and NDE bearings showed to be 150° out of phase. This phase data indicated some heavy couple unbalances in the system.

The question was: Where did the unbalances come from? New bearings were installed, along with a new balanced shaft, old impellers and sleeves, which were in running condition with 4 mm/sec rms–5 mm/sec rms amplitude. A bearing cannot cause unbalance symptoms in a pump unless mounted eccentrically. This could be ruled out because the clearances were checked, and the bearing seating area was within the acceptable limit. Shaft unbalance can be ruled out because it was a new balanced shaft with a maximum indicated run-out of 0.02 mm. Unbalanced old impellers and sleeves were ruled out, as well. The only contributing factor for unbalance could be the incorrect installation of any component. The most common error is made in the installation of the coupling



FIG. 1. Spalling on the inner ring of an angular contact bearing.

spacer. The technicians generally ignore the punch markings as a fastener mounts this on both ends. In this case, if the spacer was the culprit, there should have been more vibration amplitude on the DE side than on the NDE side, as this was a simply supported pump. The author referred to the pump's drawing for details on installation and internals.

On referring to the drawing and confirming with the maintenance technician, it was determined that each impeller was fixed to the shaft with two keys 180° apart. Pump impellers are typically balanced as a component; however, rotating one of the two impellers will produce a couple of unbalances in the system. During installation, if any one of the impellers is rotated by 180° on its axis, then the balancing of the entire rotor will be disturbed. This will produce the same signature in vibration as was witnessed (similar to coupled unbalance). Balancing a centrifugal pump can be done component-wise and as an assembly. If the impellers of this pump were balanced component-wise, rotating the impellers by 180° might not have caused this much effect (multistage pumps such as BFW pumps are generally balanced component-wise.) However, if the impellers and sleeve are balanced in assembled condition, the entire correction of the unbalanced forces of assembly is placed on the impellers. In this case, it becomes essential to adhere to the punch markings done after balancing to ensure correct mounting of components during re-assembly. Therefore, the most probable cause of unbalance could be that one of the impellers was rotated at 180° during installation.

The pump was stopped and taken into maintenance a second time. The rotor had an interstage sleeve between the impellers. This sleeve had punch markings, with corresponding punch markings on the impellers. The markings on the sleeve did not match the markings on one of the impellers, which confirmed that the impeller had been rotated by 180°. The incorrectly mounted impeller was removed.

While installing it the correct way, one of the keys was fouling. This fouling key was also one of the reasons for the error, as this key was not fouling in the incorrect assembly. During assembly, it was assumed that the impellers were to

be mounted in the position where the keys were not fouling.

initial stage or have been erased due to prolonged use, it should be

The question was: Where did the unbalances come from? New bearings were installed, along with a new balanced shaft, old impellers and sleeves, which were in running condition with 4 mm/s rms–5 mm/s rms amplitude.

The key that was fouling was finished as per the required dimension, and assembly was done taking due care of the markings on the sleeve and impellers. During post assembly, it was decided to precautionarily check the balancing of the rotor on the shop balancing machine. The rotor shop balancing was checked and found acceptable. (FIG. 2)

The post-balancing assembly check of the pump was completed and the pump was installed at the location. After taking the equipment online, vibrations were rechecked and recorded as having a maximum of 4.1 mm/sec rms.

The problem discussed in this case study could have been avoided if proper care had been given to the following:

- Punch marks on the sleeve:**

Punch markings of an impeller or any rotary component must be considered if the component is not mounted on a single key or grub screw. This error is also possible in motor external cooling fans where they are mounted on a taper bore or clamp-type mounting.

- Marking impellers:** Immediately marking impellers using permanent markers could have avoided the need for removal. Even if the punch markings are unavailable from the

a standard operating procedure to make temporary punch marks or make punch marks during disassembly.

- Double-key designs:** If double-key designs cannot be avoided, they can be made foolproof by keeping the dimensions of both keys different. Not all errors can be eliminated during the design stage. However, the best possible efforts should be made in considering maintenance practices and mistakes that could be caused due to human error.

- Assumptions.** The most critical factors of such errors are assumptions, such as presuming the impellers are individually balanced and will not cause issues if rotated, or that if the key is not entering the slot, it is not meant to enter. Most of the time, assumptions result in a waste of time, energy, resources and production. HP



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FIG. 2. Rotor mounted on balancing machine.

Sustainability through efficiency: A plan for the refining industry

The U.S. Energy Information Administration projects that carbon dioxide (CO₂) emissions will decrease through 2050 in Organization for Economic Co-operation and Development countries (OECD), which includes the U.S.¹ This projection assumes energy consumption will increase through 2050, with producers meeting these demands through a combination of traditional and renewable energy sources. Well sites and refineries can contribute to these projected emissions reductions by following the best practices outlined in this article.

Driving higher efficiency. Any facility setting out to increase efficiency must have its operations in order on all fronts. This means production must be controlled effectively with stable operation, with well-maintained equipment and safety. If there are any operational issues in these areas, management should fix these first since related costs and incidents can have far greater negative effects when compared to reductions in energy use.

This article will examine three areas where facilities can improve energy efficiency using technologies available today:

- Energy management information system (EMIS)
- Predictive emissions monitoring system (PEMS)
- Energy and mass flow management.

Based on projects where the author's company's engineers have worked in a variety of refineries, improvements can add up to 2%–3% of the relevant cost. Given the amounts a typical refinery spends on energy, these figures translate into very large numbers, with any reductions resulting in substantial increases in profitability, along with corresponding improvements to sustainability.

EMIS: Understanding energy consumption. Measurement is a critical first step to energy management because many facilities do not know enough about how they are using energy to reduce it. Obviously, the facility has an aggregate amount, but it may not be able to pinpoint the volume associated with an individual unit or specific fired heater. Let us pull this situation apart and see how to address this issue.

Energy costs at a typical refinery are among the highest, if not the highest, operating cost, often up to 50% of refining costs. The total cost comprises numerous factors related to available fuel types, individual fuel costs, equipment efficiency (boilers, fired heaters, etc.), operating conditions and a variety of other factors. To complicate matters further, at an average refinery, about 41% of energy is simply lost.

Can this situation be fixed? Yes, without question. Here is the reality: the top quartile of performers in the industry have less than one-half the energy intensity of the fourth quartile. Think about what that means. The best refineries use half the energy per volume of output than the worst. How do those top performers do it?

First, they measure energy consumption (**FIG. 1**) on a granular basis in real time. It is possible to see how much and what kind of fuel any given fired heater, boiler or other item of equipment is consuming at any time. This capability requires instrumentation and the networks to support it, with advances in wireless sensors simplifying implementation, while cutting costs. This often includes adding instrumentation to equipment currently not monitored comprehensively, or at all.

Second, all the instrumentation creates copious quantities of data that must be captured and historized. There are many platforms capable of providing visualization; however, some facilities stop here, as if data capture is an end to itself. Such programs do not deliver the desired results, requiring advancement to the next step.

Third, the data must be analyzed. This is where facilities realize the true differences in methodology and effectiveness. A basic analytical platform should cover, at least, the following five areas:

1. Validate sensors to ensure accurate measurements without noisy and faulty values.



FIG. 1. Dashboards can show energy consumption, including wasted energy, in real time.

2. Monitor key performance indicators (KPIs), displaying data on user dashboards and identifying problem areas.
3. Adjust dynamic targets based on plant states and operating modes, while identifying abnormal situations and likely process upsets.
4. Isolate root causes behind performance gaps and provide suggested corrective actions.
5. Calculate setpoints to optimize energy use at multiple operating levels, thereby minimizing cost.

The extent to which a given platform performs these functions is the main predictor of overall project success. For example, predictive models attached to dynamic targets can go beyond simply identifying abnormal situations. A truly sophisticated system should not only track these situations in real time but also offer an analysis of what is going wrong in the process (FIG. 2). In this way, the model can reach more deeply into the interactions and offer practical ways to improve operation, beyond just saving energy.

Saudi Aramco and EMIS. As a brief case in point, Saudi Aramco launched an EMIS project at its Abqaiq facility, the largest oil processing and crude stabilization plant in its fleet. The installed EMIS covered 24 production units, 57 non-production units and 237 pieces of critical equipment. Company management wanted to improve on the facility's average annual energy consumption of 30,000 Btus/bbl of oil equivalent. In addition to many concerns common to most refiners, this facility also had specific problems to solve, including:

Energy Management Functionality on Plantweb Optics Analytics

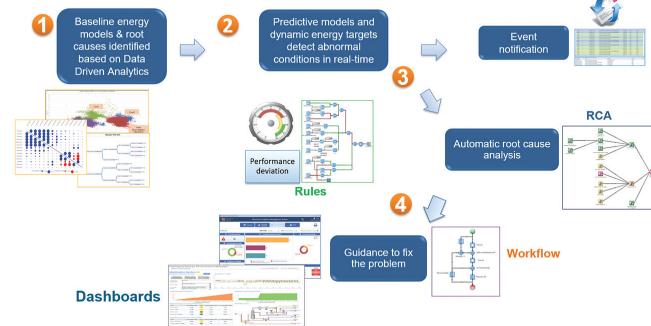


FIG. 2. An effective system does not just report data, it offers suggestions for how operators can improve operations.

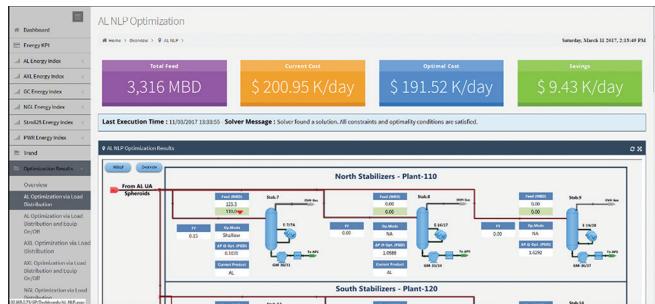


FIG. 3. This plant's system shows operators a variety of critical KPIs so they have situational awareness of energy consumption and how they can control it.

- The existing energy monitoring systems reported many false warnings of overconsumption that were difficult to troubleshoot.
- The operators occasionally found themselves operating to incorrect targets due to changes in the plant modes and states driven by a shift to a different crude source.
- The operators were adjusting loads and feeds without sufficient information to consider the full impacts on the performance of each unit and its equipment.

Engineers designing the EMIS captured the right data to analyze and solve the basic operational concerns, as well as those unique to each unit. This data was combined with dashboards (FIG. 3) configured to show critical variables, so operators could maintain critical situational awareness of process operations and energy use and then take appropriate action.

These actions were based on 13 optimization models, each of which used nonlinear programming problems and mixed-integer nonlinear programming problems methods to deliver results for minimizing the energy consumption across all plants.

The results of the project included:

- An estimated energy cost savings of \$22 MM in the first year
- An increased operational performance visibility for operators and management improved decision making at all levels
- Faster problem-to-resolution cycle time
- The best setpoints and key parameters for highest profitability retained and shared among operators.

PEMS: Extending capabilities of energy management.

Many combustion processes within a refinery are regulated by the U.S. Environmental Protection Agency (EPA) or equivalent in other countries. Such agencies require that most fired heaters, boilers and similar equipment have a continuous emissions monitoring system (CEMS) to measure and record output of various air pollutants any time equipment is in operation. Pollutants in this context can include sulfur dioxide, nitrogen oxides, carbon monoxide, CO₂, ammonia, oxygen and possibly others. The conventional solution in these cases is to deploy one and potentially more gas analyzer technologies designed to quantify the relevant pollutants for each source.

This approach can work well when applied correctly; however, it can become complex and expensive, particularly when a given installation can burn multiple types of fuels capable of producing different effluents. If there is an opportunity to save money using an inexpensive fuel for some period, but the analyzer cannot handle the likely effluents, it is a missed opportunity. Moreover, given the number of likely applications in a refinery, there can be dozens and perhaps hundreds of analyzer installations, all requiring appropriate calibration, consumables (specialized gases) and maintenance.

In many respects, the biggest drawback to this approach is how little it helps improve the process or reduce costs. CEMS analyzers are there for the sole purpose of monitoring emissions. If operators in the control room can see what they are reporting, which is usually not the case, they might get an indication that something is wrong with the combustion, but this is not always very helpful.

A better alternative is using a data-driven PEMS instead of

a conventional CEMS. A PEMS creates a model (FIG. 4) of the combustion process using data from the EMIS, historians, asset management systems or other process databases.

Since the PEMS is monitoring all relevant factors, such as fuel flow, air flow, fuel type, etc., it can calculate the effluent output in real time based on a sophisticated combustion model. The model says, in effect, given this set of operating parameters, here is the profile of effluents.

This methodology is outlined under relevant regulations, including U.S. EPA CFR 40, Part 60-61-63-75 and in the European Union under CEN/TS 17198:2018. The regulatory body will insist on evaluating a given installation to ensure the process is done correctly. Certifying an installation normally calls for a series of steps:

- Verify the application is suitable for a PEMS
- Validate sensors for accuracy and reliability
- Evaluate the emissions model's integrity
- Review documentation and training.

Once these tests are passed and the system is installed and running, the application must be tested and validated on a regular basis. Some of these will be internal checks, but the regulatory agency will participate on, at least, an annual basis with its own surveillance test.

Using a PEMS saves money over a traditional CEMS (FIG. 5) when considering both capital cost and lifetime operating cost, especially when including maintenance and consumables for conventional analyzers. However, equally as important as cost, a PEMS can work in concert with the EMIS because it is part of the larger EMIS.

Therefore, it provides insight into the process in ways that are not practical with a CEMS. It can also be part of larger process optimization strategies and energy efficiency efforts.

Mass balance: Production for energy input. The question all refinery managers should be asking is, how much product are we getting for each unit of energy input? This is a very important calculation, but it is highly complex since there are so many variables. The larger picture also includes the basic capabilities and limitations of a production unit based on conversions, yields, catalyst selectivity, fractionator cut points and energy efficiency.

An EMIS can provide the energy side of the equation, which is another benefit of such a system, but for many facilities, the weak link of examining mass balance turns out to be accurate measurements of product flows at critical points in the process.

The critical point is measuring mass flow, but in many facilities, flow instrumentation only measures volume. This is a problem because volume measurements do not take product density into account, which can lead to miscalculations. The following are several typical examples of issues:

- Since density is not measured, it is assumed to be constant, using the same value in all situations for a given product.
- Processing batches of opportunity crudes causes changes in feedstock characteristics, which can be recognized with a true mass flow reading but may be undetected if density is assumed to be constant.
- If a critical density reading is necessary, some facilities use lab analysis of grab samples; however, this does not track changing conditions.

- Converting volume to mass for high-temperature streams is troublesome since American Petroleum Institute's Volume Correction Factor tables stop at 400°F (204°C).
- Deploying density instruments in the field is possible, but there are limitations of temperature and viscous products.
- Since mass is not measured accurately, process optimization via advanced process control strategies is not practical.

Moving to mass flow measurement. Arguably, the best flow meter technology for refinery applications is Coriolis (FIG. 6). These flowmeters not only measure mass flow natively, but they also measure density directly in real time and have internal temperature compensation. Most designs include a sophisticated transmitter able to deliver the range of variables required to support mass balance calculations. In addition, they are very accurate across a wide turndown and temperature range.

Their downside is relatively high cost vs. alternate measurement technologies, along with a small internal free passage compared to the line size. Where product flows are not clean, they can be clog-prone, particularly with small line sizes. However, while cost is a consideration, the higher purchase price is far smaller than the savings realized by facilities that install them at critical points. Even a slight improvement in production can pay for the flowmeter in weeks or months.

A more common flowmeter configuration in refineries is differential pressure (dP). This technology works well in all types of installations, but it cannot provide a mass flow measurement without knowing the product's density. If the density is relatively consistent, the transmitter or automation host system can use the density value, with appropriate adjustment for

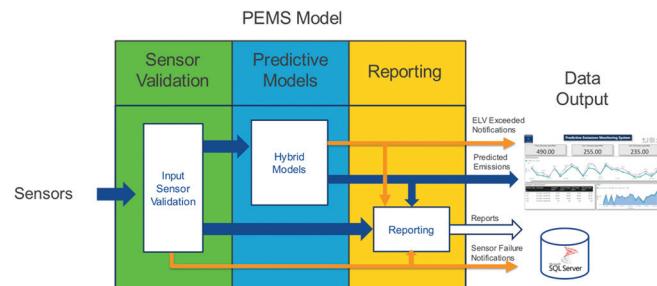


FIG. 4. A PEMS uses a process model to determine the output of pollutants from a fired heater or boiler.

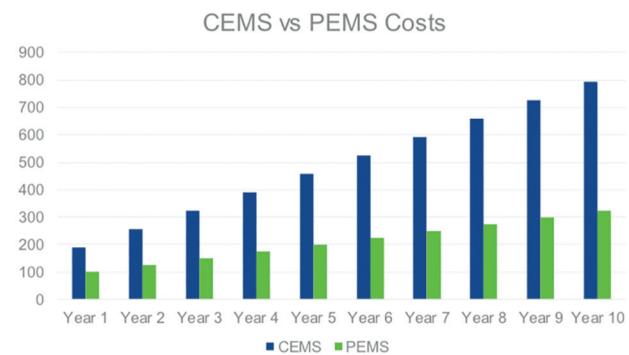


FIG. 5. A PEMS is much less expensive than a CEMS and far more versatile.



FIG. 6. Coriolis technology is usually the best choice for true mass flow readings used for mass balance calculations.

temperature, and calculate the mass flowrate. This works only when there is a temperature reading at the flowmeter, which can be part of the flowmeter or captured nearby.

For facilities and production units where there is a large installed base of dP flowmeters, there is likely a mix of reliable vs. problematic installations. Most dP installations can be improved by verifying some basic operational and maintenance considerations, including:

- How old is the transmitter? Today's dP transmitters have capabilities that were not necessarily available just a few years ago. This inexpensive upgrade can add new multivariable functions to an existing installation.
- Are the impulse lines easy to maintain? Poorly designed impulse lines can leak or clog, interfering with accurate measurements. Where sediment is a problem, they can be configured for easy clean-out.
- What is the orifice plate condition? Users should verify that the orifice edges are still sharp, the orifice is centered and it has not gotten larger due to wear. A micrometer check can be made to verify that it has not lost surface area, which would change the beta ratio.
- Does the installation have sufficient straight piping? To achieve full accuracy, dP flowmeters need straight pipe sections upstream and downstream from the orifice plate. Verify that all installations include the required length.
- When was the transmitter last calibrated? Perform whatever calibration actions are called for and check that the ranging is still appropriate for the application.

Benefits realized from mass balance efforts. Efforts designed to improve mass balance following the methods discussed can deliver major improvements to refineries. The following are three brief examples:

- With its existing measurement system, one refinery was unable to meet the $\pm 2\%$ target in its crude distillation/vacuum distillation unit. It was using dP flowmeters and one ultrasonic insertion flowmeter. It replaced 10 of the dP installations with Coriolis flowmeters, and it was then able to bring the unit

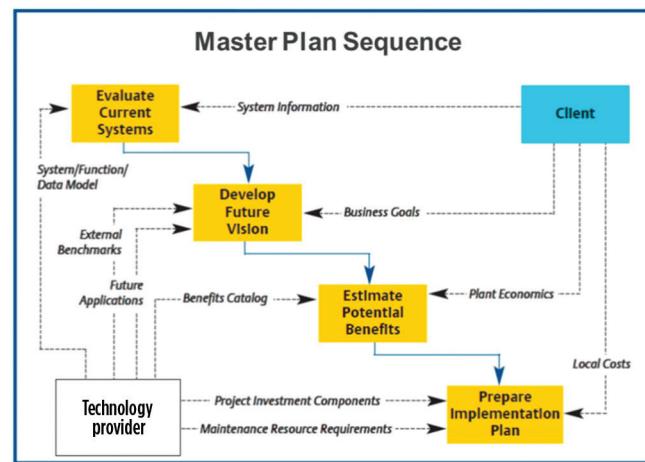


FIG. 7. A master plan ties together all elements of an efficiency project to maximize total benefits.

quickly and consistently within a $\pm 1\%$ target.

- A refinery in eastern Europe could not exceed 96% mass balance closure using dP flowmeters, even though they had been very fastidious about maintenance and calibration. They replaced nine of the most critical positions with Coriolis flowmeters. Not only did they reduce time spent on maintenance, but they were also able to improve mass balance to 99.4%.
- Another refinery had trouble stabilizing its hydrocracker due to feedstock variability. Using conventional dP flowmeters, operators were unable to accurately compensate for composition changes. By placing a Coriolis flowmeter on the main feedstock line, operators were able to recognize feedstock changes, allowing them to reach their production targets and monitor catalyst deactivation. A 2% increase in throughput was worth \$1 MM in the first year.

Tying everything together. An effective sustainability-through-efficiency project has many aspects; therefore, it requires coordination to achieve the desired goals. Each element can deliver gains on an individual basis, but when linked together through a common master plan (**FIG. 7**), truly synergistic effects can compound the benefits. Management should consider this type of plan as a key to long-term improvements capable of improving profits, reducing carbon footprint and making operations more sustainable. **HP**

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Safe and sustainable alkylation for the forward-looking refiner

In a post-pandemic economy, global governments and industry participants are increasingly committing to meeting climate action targets. Current large-scale decarbonization efforts are aimed at lowering the impact of combustion fuels on the environment.

A key pathway for meeting climate action targets entails the production of clean fuels—fuels that have lower relative carbon intensities and lower contaminant (sulfur) levels, and that are produced using pathways that result in fewer emissions or waste byproducts. Consequently, clean-burning, low-sulfur and high-performance blending stocks, such as alkylates, are becoming increasingly sought after.

This article discusses a commercial, safe and sustainable alkylation technology^a, including the performance of a 7,400-bpd brownfield unit commissioned in March 2019 at the Sinopec Jiujiang refinery.

Alkylation process. Alkylation is the transfer of an alkyl group from one molecule to another. In refining, alkylation refers to a catalytic process for producing high-value C₈ compounds, typically by reacting lower-value isobutane with C₄ olefins. Alkylate produced at the refinery is used as an octane-booster and is blended into the gasoline pool.

Traditional alkylation processes use either hydrogen fluoride (HF) or sulfuric acid (H₂SO₄) to catalyze the alkylation reaction. However, these traditional processes are inherently unsafe due to the toxic and corrosive nature of the strong acid catalysts. Refiners using acid-catalyzed alkylation technologies require ex-

otic metallurgies for process equipment, along with costly safety systems to protect refinery personnel and the public. The disposal and regeneration of spent acid catalysts have negative impacts on the environment and may pose serious chronic human health issues over prolonged exposure.

The referenced alkylation technology^a is an inherently safe process that uses a proprietary composite ionic liquid (CIL) catalyst to facilitate the alkylation reaction. CIL catalyst is a non-volatile, non-aqueous liquid salt that is formulated by modifying a chloroaluminate ionic liquid platform with a transition metal. The composite nature of the CIL catalyst allows the process to enhance alkylate product selectivity and to overcome residual corrosion issues typically associated with ionic liquid catalysts. CIL cata-

lyst is non-hazardous and non-corrosive, allowing all alkylation process equipment to be manufactured using carbon steel. This catalyst can also be regenerated in-situ under moderate operating conditions, which provides added benefits of safe handling and emissions reductions vs. alternative technologies.

Alkylation market outlook. Although world oil markets have rebounded from a sharp decline in demand caused by the global pandemic, experts believe that policy-driven factors may lead to peak oil demand sooner than previously thought.¹ The International Energy Agency (IEA) forecasts that total gasoline demand is unlikely to return to 2019 levels, due to efficiency gains and a shift toward renewables.²

In developed economies, the shift to



FIG. 1. View of a brownfield 7,400-bpd CIL-catalyzed alkylation unit at Sinopec Jiujiang Co.'s Jiangxi plant.

electric vehicles is expected to significantly impact the long-term demand for gasoline. However, despite the macro changes in gasoline demand, the alkylate outlook remains stable, offset by an increased demand for higher-performance fuels for high-efficiency engines.

Existing acid-based alkylation infrastructure is aging and represents a growing safety and financial risk for the modern refiner. In the wake of a bankruptcy-causing 2019 HF alkylation unit explosion at a U.S. refinery,³ the rising costs of insurance and safety are driving refiners to consider inherently safer alternatives.⁴ In the U.S. and Europe, opportunities for implementing this CIL-catalyzed alkylation technology^a are in the

replacement, modernization and safety enhancement of the legacy acid-based alkylation processes.

In emerging or transitioning economies, robust mobility growth in the populace is expected to continue to drive modest gasoline demand for the next decade. In developing markets, the opportunity for implementing the CIL-catalyzed alkylation technology^a is in greenfield projects or expansions of brownfield projects.

Commercialization and scale-up. This CIL-catalyzed alkylation technology^a has been under development for two decades. Beginning with a 0.5-bpd continuous pilot testing project in 2003, the technology has been scaled up to a commercial production capacity of 7,400 bpd.

In 2005, the first commercial field demonstration was successfully performed at the PetroChina Lanzhou refinery by retrofitting an existing H₂SO₄ alkylation unit with CIL catalysts.⁵ In 2013, Deyang Chemical Co. Ltd., an independent refiner, commissioned a greenfield 2,450-bpd unit.⁶ In 2018, PetroChina Harbin Petrochemical Co. Ltd. implemented the technology in a brownfield operation at a scale of 3,700 bpd.⁷

Between 2017 and 2018, the Sinopec group licensed the CIL-catalyzed alkylation technology for three installations (the Jiujiang, Wuhan and Anqing refineries), each at a scale of 7,400 bpd.⁸ Construction for the units was completed

between 2018–2020. Notably, the Sinopec Wuhan unit was a revamp from an existing HF-based alkylation process—representing a major milestone and an industry first.⁹

Commercial process performance.

The following section discusses the recently commissioned brownfield 7,400-bpd CIL-catalyzed alkylation unit at Sinopec Jiujiang Co.'s Jiangxi plant (**FIG. 1**), which has a process operating flexibility of 60%–110% and occupies a plot space of 126 m x 74 m. The unit is designed to handle mixed olefin feedstocks from both methyl tertiary-butyl ether (MTBE) and fluid catalytic cracking (FCC) units.

The turnkey capital cost for the unit (including engineering, procurement, construction, commissioning and inspections) was approximately \$78 MM and included the installation of four key sections: a feed pretreatment system, a reaction system, a catalyst regeneration system and a product separation/purification system. Sinopec Engineering Construction Co. Ltd. led the engineering aspects of the project, while Sinopec Nanjing Engineering Co. undertook the construction works.

After 1 yr of construction, mechanical completion was achieved in 4Q 2018, and the unit was commissioned 1Q 2019. In 2Q 2019, the operator conducted a calibration test to benchmark and compare commercial process performance data against design specifications and to identify optimization opportunities. At the time of this publication, no safety-related incidents or concerns have been identified by the operator.

TABLE 1 compares the commercial and design feed compositions. Although the isobutane content of the commercial feed (39.7 wt%) was comparable to that of the design basis (38.5 wt%), the total C₄ olefin content of the commercial feed (32.7 wt%) was significantly lower than expected (46.3 wt%). Further, the non-reactive n-butane content in the commercial feed (25.6 wt%) was significantly higher than the design basis (14.8 wt%), and the commercial feed also contained contaminates, namely 1,3 butadiene and methanol.

The CIL-catalyzed alkylation technology^a is intended to stoichiometrically react isobutane with C₄ olefins. The design basis anticipated that C₄ olefins feedstock would be supplied in excess relative

TABLE 1. Feed compositions

Constituent	Design	Commercial
Propane, wt%	0.1	0.8
Propylene, wt%	0.3	0.9
Isobutane, wt%	38.5	39.7
N-butane, wt%	14.8	25.6
1-butane, wt%	11.8	11.4
Isobutylene, wt%	11.6	0.2
Trans-2-butene, wt%	9	12.6
Cis-2-butene, wt%	13.9	8.5
Isopentane, wt%	0	0.1
1-pentane, wt%	–	0.2
1,3 butadiene, ppm	–	1,081.5
Methanol, ppm	50	225

TABLE 2. Mass balances

	Stream	Design, tph	Commercial, tph
Feed	Mixed C ₄	37	39.68
	Hydrogen	0.08	0.04
	Saturated LPG	5.23	0
	Supplementary isobutane	3	0
Total		45.31	39.72
Products	Alkylate	35.85	27.2
	Isobutane	0.7	3.79
	N-butane	6.18	7
	LPG	1.63	0.78
	Fuel gas	0.9	0.09
	Acid soluble oil	0.05	0
	Flare gas	0	0.86
	Total	45.31	39.72
	Alkylate yield	79%	68%

to isobutane. In commercial operation, however, the opposite occurred—isobutane was supplied in excess relative to the C₄ olefin content.

TABLE 2 compares the commercial and design mass balances and alkylate yield. The design basis required a supplementary isobutane stream (3 tph) to fully react with C₄ olefins that were in excess in the design feed. The commercial application did not require utilization of the supplementary isobutane stream. Due to the commercial feed containing relatively lower quantities of C₄ olefins, excess isobutane and relatively higher quantities of non-reactive n-butane, the alkylate production and yield underperformed compared to the design case. As a result, the effective alkylate production rate for the unit was 5,600 bpd, as compared to the designed 7,400 bpd.

In commercial operation, 0.86 tph of flare gas was produced, representing 2.2 wt% of the feed. The flare gas was attributed to unrecovered isobutane, which, under the design scenario, was intended to be captured and recycled using the compressor system flash tank. As isobutane in the commercial feed was supplied in excess, the original design load of the recovery system was insufficient to handle the additional throughput; therefore, flaring was required. At present, a corresponding retrofit scheme has been proposed to add a pumping system to increase the recovery capacity of flashed isobutane.

It should be noted that the deviation in feed composition of commercial feed from that of the design feed experienced by the operator is not unusual, since the typical feedstocks for the alkylation process are off-gases from upstream FCC or MTBE units. The off-gas compositions are dependent on FCC/MTBE feed and their operating conditions.

TABLE 3 compares the commercial and design alkylate product specifications. Key metrics—such as the research octane number (RON), motor octane number (MON) and endpoint distillation temperature—met the design basis specifications during commercial operations, indicating that the process produces superior-quality alkylate. The observance of a higher commercial product Reid vapor pressure (RVP) was due to the operator's inclusion of up to 10 wt% n-butane alongside alkylate prod-

TABLE 3. Alkylate product specifications

Specification	Design basis	Commercial
RON	96.5 ± 0.5	97.5
MON	94 ± 0.5	95
Initial boiling point, °C	Unspecified	37
10% distillation temperature, °C	Unspecified	80
50% distillation temperature, °C	Unspecified	105
90% distillation temperature, °C	Unspecified	113
Endpoint, °C	≤ 200	168
Vapor pressure (37.8°C), kPa	35	46.6
Density (20°C), g/cm ³	0.69	0.7
Chloride content, ppm	< 1	0.3
Sulfur content, ppm	Unspecified	< 0.2

TABLE 4. Alkylate composition

Constituent, wt%
C ₃
C ₄
C ₅
C ₆
C ₇
C ₈
C ₉
C ₁₀
C ₁₁
C ₁₂

uct to balance the low RVP in the plant's existing gasoline pool. Modifying the n-butane content in the alkylate product was achieved by adjusting the process operating conditions of the n-butane extraction column. Complete removal of the n-butane fraction from the alkylate product would result in an alkylate RVP of less than 30 kPa.

TABLE 4 shows the composition of the commercial alkylate product. The process achieved 100% olefin conversion. No C₁₂⁺ or higher boiling point compounds were detected in the product stream. The C₈ content in the alkylate was 82%, which is comparable to, or exceeding the performance of, best-in-class competitive acid-based alkylation processes. The narrow distribution of the alkylate composition indicates that the process is highly selective for alkylate yield.

TABLE 5 shows the commercial utilities consumption for the unit. The absolute consumption rates for steam, electricity, instrument air and recycled

TABLE 5. Utilities consumption

Utilities	Commercial quantity
1 MPa steam, tph	36.88
3.5 MPa steam, tph	3.21
Electricity, kWh/hr	5,480
Instrument air, Nm ³ /hr	199.67
Recycled water, tph	1,801.54
Condensed water discharge, tph	-40.09
Total, kgEO/t alkylate	154.51

TABLE 6. Recommended contaminant limits

Contaminant	Limitation, ppm
Water	≤ 10
Butadiene	≤ 50
Methanol	≤ 50
Dimethyl ether	≤ 100
MTBE	≤ 50
Total sulfur	≤ 20

water were in alignment with other operators using the CIL-catalyzed alkylation technology^a. However, when energy use was normalized to kilograms of oil equivalent (kgEO) per ton of alkylate produced, the energy consumption for this installation (154.51 kgEO/t alkylate) was 20%–30% higher than the peer group, as expected. The discrepancy was attributed to the lower-than-anticipated alkylate production due to feed quality issues (low olefins and high non-reactive n-butane contents). The operator has identified feed control as an area of optimization and is considering measures to

TABLE 7. Consumables

Item	Design basis	Commercial
Catalyst active reagent, kg/hr	232	150
Organic chloride activator, kg/hr	19	12
30% NaOH, kg/hr	300	150
Total consumables, kg/hr	551	312

increase the feed olefin content to maximize alkylate production.

TABLE 6 lists the licensor-recommended contaminant limits for the process, and **TABLE 7** compares the commercial and design consumables for the process. While processing feed with higher contaminant levels does not impact the safety or operation of the unit, the catalyst consumption rate may increase. Therefore, a feed-dependent pretreatment configuration is recommended for each installation.

During regular operations, the majority of spent CIL catalysts are regenerated onsite in the regeneration unit, and catalyst activity is maintained through the addition of an organic chloride activator compound. A 30% sodium hydroxide (NaOH) solution is used to remove feed contaminant sulfur via caustic wash and to secondarily neutralize small quantities of spent catalyst byproduct prior to disposal. A roughly equal quantity of catalyst active reagent is added to offset spent catalyst removals.

Despite the methanol content in the feed being in excess of the licensor-recommended limits, the commercial operation required 43% fewer total consumables than the design basis. A key reason for the lower-than-anticipated consumables was the presence of higher quantities of non-reactive n-butane in the commercial feed alongside lower quantities of olefinic reaction materials. It is expected that future modifications to the feed aimed at increasing the alkylate production rate will bring the commercial and design estimates closer to alignment. The future addition of a pretreatment methanol removal unit may present an opportunity to further reduce catalyst consumption.

Takeaway. The CIL-catalyzed alkylation technology^a is a commercially proven high-performance alkylation process that meets the health, safety and environmental objectives of stakeholders. As with any newly implemented tech-

nology, a retrospective review of initial process performance indexed against the design basis provides an excellent opportunity to identify optimization and debottlenecking projects, and such a review should be undertaken within the first 6 mos of commissioning.

Lessons learned from commercial experience highlight the importance of selecting a robust alkylation technology that has a high tolerance for feed composition variability, accurately predicting feed characteristics during the design phase of the project, while also ensuring stable feed during commercial operations. Significant deviations and fluctuations in the feed may result in variations in the alkylate yield, energy consumption per quantity of alkylate produced and consumables required. Nonetheless, the CIL-catalyzed alkylation technology^a is demonstrated to consistently produce high-quality alkylate in a safe and sustainable manner. **HP**

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NOTE

^a Ionikylation is a CIL-catalyzed alkylation technology developed by the China University of Petroleum—Beijing and licensed worldwide by Well Resources Inc.

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Shrinking the carbon footprint: A digital transformation roadmap for green fuel producers

From ethanol and renewable diesel to biofuels and gas-to-liquids, the world is moving toward low-carbon energy sources to mitigate climate change and boost energy security. These new sources of energy have their own challenges; the key to meeting those challenges lies in the ability to optimize processes and systems.

However, before any organization can optimize processes and systems, it first must recognize that data is a critical asset and, as such, requires proper management. Many green fuel companies already have existing or planned ecosystems of control and data systems across their operations based on tags. These tags contain sensor data such as temperature, flows and vibration. However, all this data is meaningless if it is not contextualized. In fact, a wealth and diversity of tags, without structure or context, becomes a roadblock to discovering valuable insights. A high quantity of data is only as useful as its quality allows. All the promises of big data and the digital transformation will remain out of reach if data is not structured and contextualized, which is not an easy task in traditional information technology (IT) data lakes.

Because consistency in calculations and operations data transformation is key to generating actionable intelligence from data, the most progressive companies are adopting operations data infrastructures that normalize disparate data sources and enable subject matter experts (SMEs) to add context and lower-level analytics. This generates maximum efficiencies and profitability in a competitive environment where subsidies and incentives will not always be available.

How operational intelligence drives optimization. An operational data infrastructure gives site operations SMEs the ability to configure performance dashboards, which SMEs can then use to make proactive, better informed decisions to keep plants running smoothly. Smarter decision-making means improved efficiency, reduced operations costs, reduced maintenance costs and fewer lost opportunities.

Digitally optimizing work processes also grants engineers access to previously inaccessible data, with exceptional accuracy and little-to-no delay. Even at a very basic level of implementation, digital transformation projects reduce operators' rounds, increases situational awareness and allows operators to prevent and respond to abnormal operations and events. In turn, these improvements promote safety, operational performance and reduce carbon and greenhouse gas (GHG) emissions.

Custom dashboards provide end users better visibility into

operations, which allows them to both improve their business relationships and increase their return from the digital value chain.

Carbon accounting: A new currency. Green fuels may be the solution to minimizing carbon emissions, but they also pose new challenges. By the old energy paradigm, the oil and gas industry focused single-mindedly on achieving the lowest production cost. Today, that focus is complicated by a second, competing priority to achieve the smallest carbon footprint.

The goal is not just to minimize GHGs at one refinery but across the entire supply chain. One of the biggest opportunities that an operational data infrastructure affords is the creation of a digital value chain—the ability to securely share operations data with key stakeholders across the supply chain to optimize efficiency and minimize carbon footprint.

For example, some green fuel companies are now sharing their operations data with catalyst providers, which run near-real-time modeling of production processes to identify possible improvements. In other cases, green hydrogen producers purchase electricity needed in the refining process from green vendors, such as wind and solar farms. These types of collaborations, which contribute significantly to overall net-zero goals, are only made possible by the accessibility and shareability of critical carbon accounting data.

In the same way that companies exchange dollars and euros, green fuel producers are now exchanging carbon credits as part of their daily operations. This ability is an increasingly important factor in risk management and investment decision-making. Exchanging carbon credits requires transparency, consistency and verifiability. As blockchain and similar technologies evolve, operations data infrastructures are becoming more essential in calculating those carbon credit values in such a way that they can be bought, sold and traded. An operations data infrastructure also produces insights that can help optimize enterprise-wide financial reporting.

Digital pitfalls to avoid. Some companies simply send all their data to data lakes, typically hosted by cloud vendors. By this imperfect strategy, the resulting data lacks context and consistency. Simultaneously, the volume, velocity and variability of data output in an era of increasingly smart devices can quickly become overwhelming. Just one data source—such as a wind turbine or a piece of refinery equipment—can generate tens of thousands of data points every few seconds. When concerns about cybersecurity and governance are added to the equation, it becomes clear

that the data lake is a less-than-ideal solution. For significantly better results, businesses should consider a hybrid approach that pairs a purpose-designed operations data infrastructure—securely in a single-tenant cloud—with a cloud-based software as a service (SaaS) solution, so that data is accessible and shareable.

Another common pitfall to avoid is that many companies reach for Big Data applications before they have secured a strong data foundation. Digital twins, machine learning (ML) and artificial intelligence (AI) all reside in a layer of advanced analytics that can generate significant value but typically produce poor results if a robust analytical framework is not already in place.

Once a green fuel company has installed an operations data infrastructure, they should implement descriptive, diagnostic and simple predictive analytics. From there, operators can begin using prescriptive and adaptive analytics that incorporate ML and AI. Once green fuel companies reach this level of advanced analytics, it is important to funnel those results directly back into operations to enable even more optimization.

The following is an example of how that happens. A furnace is used for heating oil during the refining process. Operators work to optimize heat output, while minimizing carbon emissions. They start by modeling the furnace and applying lower level analytics to examine the correlations between pressure, feed and fuel composition, temperature, excess air, and oxygen content from analyzers. Once operators have a foundational understanding of the process, more advanced technology can be added that uses laser-based sensors to increase the accuracy of the oxygen

and carbon monoxide content in the excess air. Finally, AI pulls all those factors together to calculate the changes necessary to further improve processes. That information is then sent back into the system so that operators can adjust in near real time.

These same principles can be applied to projected vs. actual results (i.e., projected GHGs vs. actual GHGs).

The key to implementation. Those who deal in operational technology (OT), which is designed to run refineries safely and optimally, and IT, which focuses more on streamlining back-office operations, often clash when it comes to digital investments. The IT department—which is expected to be the steward of technology across the company—typically applies a traditional IT mentality to operations, but IT departments rarely appreciate the nuances of operations data and systems.

A typical IT-style solution to data management might see all operations data dumped into a data lake. Operators will then apply AI to this reservoir of unstructured, decontextualized data. This is, in other words, a combination of two mistakes discussed earlier. Not only does this practice produce very little in the way of valuable insights, but it can also result in several lost opportunities.

Companies that excel at digital transformations have redefined this OT-IT relationship by installing a Chief Digital Officer or Chief Transformation Officer, with a deep operational background. By overseeing both OT and IT, a Chief Digital Officer has a unique vantage from which to normalize operations across both departments. Such an officer is also well-positioned to drive sustainable business change by leveraging new digital technologies.

No digital transformation initiative should be an all-or-nothing commitment. Until a company learns what works, the best advice is to start small, simple and strategic. The key is to start.

Companies should begin with a relatively bounded operational area—one that is a likely candidate for success. For example, companies might begin by increasing the runtime of heat exchangers before fouling, or they might compare several installations of a given asset type in search of outliers. Starting small helps green fuel companies apply their digital strategies appropriately and demonstrate business value clearly. To prove the success of the business case, companies will need to identify key performance indicators by which to measure and document conditions before and after. In a sense, this is using data to show the value of that data.

To remain competitive over the long term, green fuel producers must continually strive for operational excellence; they must have a business model that is viable even without subsidies; and they must embrace modern carbon accounting. A digital-enabled business transformation, underpinned by an operations data infrastructure, is the key to achieving these goals. **HP**



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IMO 2020 impact assessment study on KIPIC Al Zour Refinery future operations

What is IMO 2020? As of January 2020, the International Maritime Organization (IMO) has mandated that sulfur shipping emissions must be reduced: the regulation states that sulfur specifications for fuel oil (bunker) have been reduced from 3.5% (35,000 ppm) to 0.5% (5,000 ppm). The main purpose of the regulation is to prevent acid rain and lower the environmental effects.

Shipowners must switch fuel from high-sulfur fuel oil (HSFO), which has a sulfur content of 3.5%, to very low-sulfur fuel oil (VLSFO), which has a sulfur content of 0.5%, marine gasoil (MGO), install scrubbers, or convert to liquefied natural gas (LNG)-powered systems (FIG. 1).¹ While scrubbers can burn HSFO and extract the sulfur from it, ordering and installing scrubbers in ships can take as long as 8 mos–13 mos. The last option for ships is to convert to LNG, which is costly and presents uncertainties in future supply and demand.² One thing is certain: the increased demand for fuels with lower sulfur content is affecting and changing the global market.

IMO 2020 impact on refineries. The IMO 2020 will have a major effect on refineries of all configurations. Topping refineries, which use fuel as their main product, are considered the least complex configuration for refineries. Producing high quantities of HSFO when processing high-sulfur crudes means that they must switch to lower sulfur crudes (e.g., light sweet crudes) to meet specifications and produce VLSFO. If the refinery is unable to meet these specifications, it will have to sell the HSFO and accept the lower product demand and prices.³

Cracking refineries are medium-complex refineries that contain such units

as catalytic crackers and hydrocrackers. They also produce fuel oil but have more options to produce lighter products to be utilized in other processes. Full-conversion refineries are considered the most complex and have more options than topping and cracking refineries. They produce a small quantity of fuel oil, and can switch between crudes and produce higher quantities of lighter products based on demand.⁴

For these refineries, options exist to meet IMO 2020 regulations, including:

- Changing the crude slate to sweet crudes
- Adding secondary processing units, which can take years to build
- Revamping units to produce lighter products with low-sulfur content
- Producing MGO as the main supplier for fuel for ships
- Blending lighter products with fuel oil to meet the fuel specifications.

Predicted prices before 2020. Many refiners began switching to produce VLSFO and MGO prior to the implementation of IMO 2020. Prices for sweet crudes with low-sulfur content were predicted to rise due to anticipated high demand to meet the specification, while prices for sour crudes with high-sulfur content were predicted to fall.⁴ Prices for VLSFO and MGO were also forecast to rise, with MGO prices increasing more than VLSFO in conjunction with higher diesel demand.

VLSFO pricing was anticipated to increase by 11%–23%, while one report predicted that the price increase could be as high as 50%.¹ HSFO, which comprises 70%–80% of the price of crude oil, was predicted to decline at the beginning of 2020.⁵ It was predicted that refineries that produce high quantities of diesel and low-sulfur fuel oil would gain significant margin growth for those products, as they were producing a blend of gasoil and fuel oil to meet the 0.5% sulfur requirement.

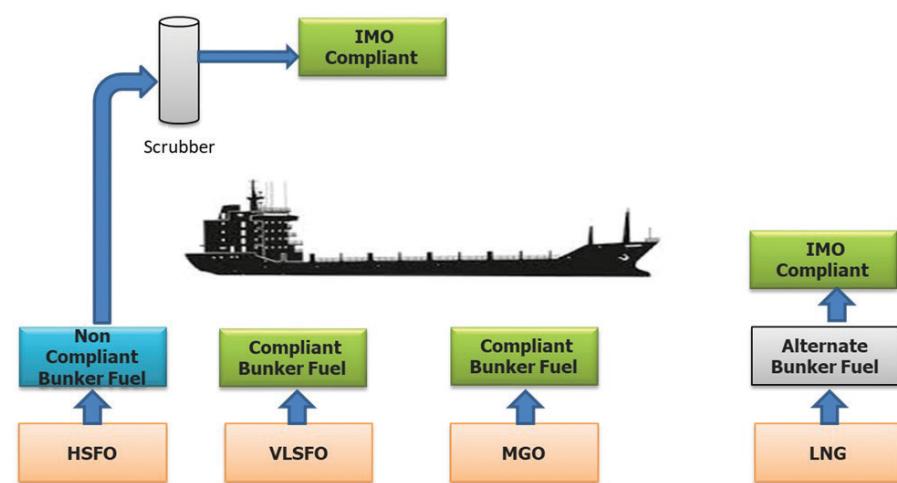


FIG. 1. Types of fuel that can be used as bunker.

Actual prices in 2020. The year 2020 began strong, as researchers predicted, with VLSFO and MGO reaching their peak prices. By January 8, VLSFO had reached \$686.50/metric t (tonnes), MGO reached \$732/metric t, and HSFO prices remained stable at \$407.50/metric t, based on the global average bunker pricing.⁶

However, by February 2020, the prices for these products fell—MGO prices fell almost 9% and VLSFO prices fell approximately 12%. This is attributed to the significant quantities of LSFO (i.e., VLSFO or a mixture of diesel and fuel oil) in the market at that time.⁷ Of course, it is impossible to deny the effects on global markets caused by the COVID-19 pandemic and the World Health Organization (WHO) declaration of a global health emergency. The havoc and tragedy caused by COVID-19

spread rapidly throughout the world—travel was limited globally and many consumers were required to stay home, so prices and demand for crude oil and other products began to sharply decline.⁸

To exacerbate the problem, a crude oil price war began between the Organization of the Petroleum Exporting Countries (OPEC) and Russia over oil production cuts, leading to breaks within the OPEC+ alliance.⁸ These factors led to a sharp decline in the prices of crude oil, VLSFO, MGO and HSFO (shown in FIGS. 2 and 3). On April 20, the WTI crude price dropped below \$0/bbl due to limited storage capacities and low liquidity;⁹ by the end of the month, the crude prices of Brent, Kuwait Export Crude (KEC) and WTI fell to an average of \$18/bbl,¹⁰ the lowest in years (FIG. 2).

VLSFO and MGO pricing fell to \$272/metric t and \$400/metric t, re-

spectively, (FIG. 3) which is a loss of approximately 60% for VLSFO and 53% for MGO from the first week of 2020.⁶ By May 1, the crude oil price war ended and prices began showing an upward curve, reaching \$72.99/bbl for Brent, \$72.61/bbl for KEC and \$68.50/bbl for WTI by the end of August, an increase of approximately 300% for Brent and KEC and 280% for WTI since their April 2020 prices. VLSFO and MGO prices reached \$567.5/metric t and \$663/metric t, respectively—still a drop from the beginning of 2020, but a gain of 108% and 66%, respectively, from their low numbers in April 2020. FIGS. 2 and 3 highlight the fluctuating trends of crude oil, VLSFO and MGO prices since the beginning of 2020.^{11,12}

Note: The OPEC+ countries have agreed to increase their production by 400,000 bpd beginning in May 2022, which will create a huge effect on the oil and gas markets, from crude oil to its petroleum products.

KIPIC. Kuwait Integrated Petroleum Industries Co. (KIPIC) is a subsidiary of Kuwait Petroleum Corp. (KPC) set up by the State of Kuwait to manage refining, petrochemicals, integrated refining and petrochemicals operations, and LNG supply that maximizes shareholder value and achieves LNG import operations in the Al-Zour complex.

Al Zour Refinery. Al Zour Refinery is designed to process 615,000 bpd of crude oil. The facility comprises three topping refineries of equal capacities and three atmospheric desulfurization units (ARDSs) for processing atmospheric residue.

The key objectives of the refinery are to satisfy future Kuwait Ministry of Electricity and Water (MEW) LSFO demand, with the remaining quantity to be used for export and internal con-

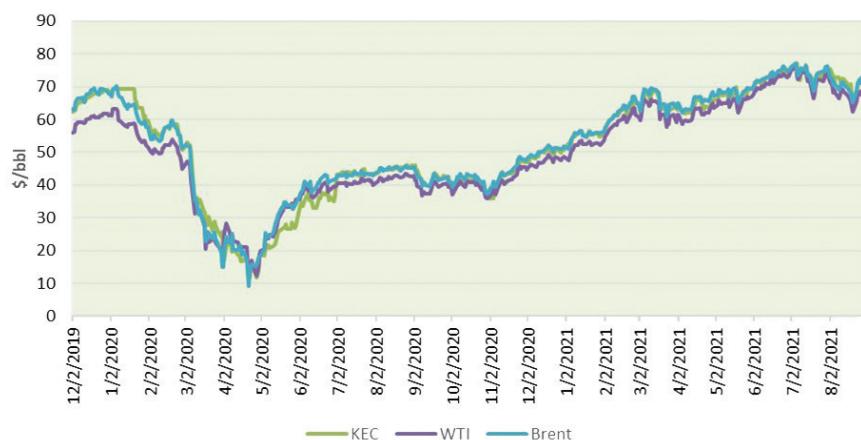


FIG. 2. Crude oil prices.¹⁰

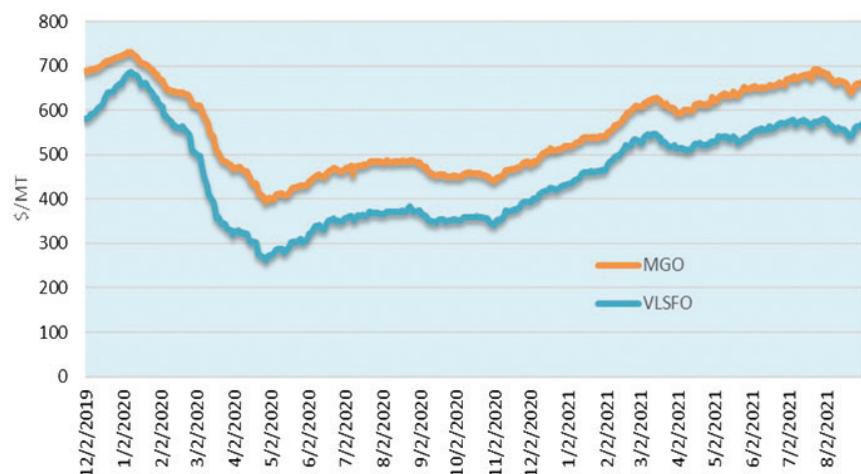


FIG. 3. MGO and VLSFO prices.

TABLE 1. ARDS stream properties

Sl no	Properties	ARDS stream
1	Specific gravity, g/cc	0.9292
2	Sulfur, wt%	0.5
3	Viscosity cSt at 50°C	175
4	Nickel + vanadium, ppmw	10.4
5	Asphaltenes, wt%	2.3

sumption; satisfy the fuel oil requirements for use within the new refinery; and produce light products meeting long-term specifications. The combined total fuel oil production, including an estimated internal fuel oil consumption of 9,300 bpd, is 234,000 bpd.

Al Zour Refinery is designed to produce 1 wt%-sulfur LSFO for the MEW while producing 0.5 wt%-sulfur VLSFO for internal fuel and export.

Fuel oil production and facilities. Al Zour Refinery is a topping refinery with fuel oil production coming from the ARDS, crude distillation column bottom and property corrections using distillate yields, as required. The fuel oil production is illustrated in FIG. 4.

The refinery has three 205,000-bpd crude distillation units (CDUs) and three identical 110,000-bpd ARDSs. Each ARDS train has two identical 55,000-bpd reaction trains. The refinery is designed to process 100% of the atmospheric residue. TABLE 1 shows the properties of fuel oil produced from the ARDSs, confirming that Al Zour Refinery can produce the VLSFO from each ARDS.

CASE STUDIES

Various factors affecting refinery operations, profitability and optimization upon implementation of IMO 2020 have been studied. The different scenarios for each factor are detailed here.

Types of crude. Al Zour Refinery is designed to process four distinct types of crudes: KEC, Kuwait Heavy Crude (KHC), Lower Fars and Eocene. Scenarios with different crude mixes, as well and their impact on refinery throughput and fuel oil production, were studied. The ARDS is designed to process two types of feed: light crude and mixed crude.

- Light crude refers to the residue coming from the CDU operating with 100% KEC.
- Mixed crude refers to the residue coming from the CDU, resulting in a mixture of 25.5 wt% Eocene, 38.2 wt% KHC and 36.3 wt% KEC (TABLE 2).

Therefore, TABLE 3 shows that Al Zour Refinery is equipped to manage both crude mixes and does not need a crude reduction due to the new VLSFO specification.

Economically, it should be noted that mixed crude processing will be a superior feed for the ARDSs.

Refinery units shutdown scenarios.

The following scenarios are considered:

1. Normal operation of the CDU

and ARDS (no shutdown). A CDU turnaround is considered only once every 6 yr, as per design. An ARDS shutdown is considered every year for catalyst changeover. After the first year, one train will be under a service

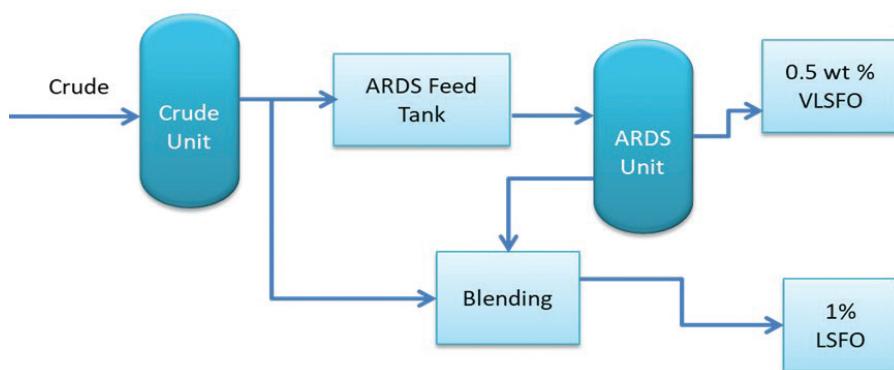


FIG. 4. VLSFO production at Al Zour Refinery.

TABLE 2. Types of crude oil in Kuwait

Name	Kuwait Export Crude (KEC)	Kuwait Heavy Crude (KHC)	Lower Fars Crude	Eocene
API gravity	30.3	24	14.5	17.7
Specific gravity	0.9	0.9	1	0.9
Total sulfur, wt%	2.6	3.6	5	4.4
Asphaltenes, wt%	2.3	5.5	7.1	5.6
Basic nitrogen, ppmw	394.1	561	586.6	609.5
Nickel, ppmw	10.9	19.4	26.7	16.5
Total nitrogen, ppmw	954.5	1,828.2	1,872	1,341.5
Vanadium, ppmw	31.5	43.6	95.1	49.4

TABLE 3. Case studies on impact of various types of crude processing

Sl. No	Factors	Light crude	Mixed crude
1		205,000 bpd KEC in CDU-01	205,000 bpd KEC in CDU-01
2	Total crude throughput design	205,000 bpd KEC in CDU-11	210,000 bpd KHC in CDU-11
3		205,000 bpd KEC in CDU-21	120,000 bpd Eocene in CDU-21
4	Design CDU operational availability	96.60%	96.60%
5	Total crude charge	615,000 bpd	535,000 bpd
6			KHC - 49.6 %
7	Atmospheric bottom (ATB) yield	KEC - 49.6%	KHC - 58.1%
8			Eocene - 68.1%
9	Total ATB production	303,200 bpd	305,400 bpd
10	Total ARDS capacity	330,000 bpd	330,000 bpd
11	ARDS residue yield	78.50%	80.30%
12	Total LSFO production from ARDS	238,100 bpd	245,200 bpd

factor for catalyst changeover every 2 mos. Therefore, if no emergency shutdown occurs, there will be no shutdown during the first year of operation. In a mixed crude case, if all ARDS trains are available, the ATB processing capacity (55,000 bpd \times 6 = 330,000 bpd) is higher than its production (305,400 bpd) from the crude columns. In this case, the entire ATB will be routed to ARDSs to produce 0.5% sulfur VLSFO without bypassing the ARDSs. The VLSFO production for MEW/export is expected to be 235,240 bpd after an internal consumption of 10,000 bpd.

2. **Normal operation of the CDU and ARDS shutdown for catalyst changeover.** A one-train shutdown of an ARDS for a period of 25 d is considered, as per design. The ATB processing capacity at the ARDS (55,000 bpd \times 5 = 275,000 bpd) is lower than its production (305,400 bpd) from the crude columns. No ATB bypass is required to meet 0.5% sulfur specifications: around (30,400 bpd \times 25 d) 760,250 bpd of ATB will be required to be stored over this shutdown duration, which can be processed later when the unit is back in operation. Total VLSFO production for MEW/export is estimated to be 210,830 bpd during this period.
3. **Normal operation of the CDU and emergency shutdown of ARDS.** The ARDS will be required to run continuously at maximum capacity since each ARDS train will be out for catalyst replacement each alternating month. Any unplanned upset affecting ARDS availability will require CDU throughput reduction.

The cases are evaluated considering mixed crude processing.

Upgradation/modifications required in the existing configuration. Considering these cases, it was concluded that no modifications to the existing process

units facility are required to meet the new IMO specification. However, the operational flexibility of the refinery is highly compromised and the handling of dual qualities is extremely challenging. Hardware modifications in shipment lines/tankage are required to produce two grades of fuel oil.

It is planned to evaluate alternate catalyst for ARDSs, along with modifications in the refinery line-up for handling two grades of fuel oil specifications.

Additional chemicals required. No additional chemicals or additives are required to meet the new IMO specification. However, the use of a hydrogen sulfide (H_2S) scavenger additive can be optimized or stopped in view of non-blending of high- H_2S streams—such as CDU residue from high-sulfur crudes like KHC, Eocene or Lower Fars—to the new product.

Blending facilities. With the implementation of the new specification, bunker fuel oil will become a straight-run product rather than a blended product. Note: the high-sulfur content of CDU residue makes it impossible for blending; so, with the current configuration, no additional blending facilities are required.

Takeaway. The IMO 2020 regulation has affected both shippers and refiners: shippers must upgrade their ships by installing scrubbers to process the HSFO or use VLSFO as their bunker; and refiners must adapt by installing new units, changing the crude slate or blending light products with fuel oil to meet the specification. The regulation is being met with high demands for VLSFO, which made its price rise by the beginning of the year 2020.

The regulation on reduced sulfur will be beneficial for KIPIC refinery margins. From the unit product specification and shutdown scenarios, it can be noted that no additional modifications are required for meeting the new specification. With the increased focus on operational availability and reliability of the ARDS, KIPIC capacity utilization is expected to be more than design and, therefore, reap the benefits of the new regulation.

Further modifications in the future for sulfur content in fuel oil will cause

KIPIC to either revamp their ARDS or change the activity of the catalyst to meet the specification. Pricing for crude oil, VLSFO and other products will continue to rebound. Future studies can examine the market after the crises are over and if new IMO regulations are applied. **HP**

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Taking a measured approach to climate change through continuous emissions monitoring systems

The need to reduce emissions has never been greater. A report¹ published by the Inter-governmental Panel on Climate Change (IPCC) has been labeled a “code red for humanity” by the United Nations (UN). The report highlights that the Earth’s surface temperature was 1.09°C higher in the decade between 2011–2020 than between 1850–1900, that the past 5 yr have been the hottest on record since 1850, and that the recent rate of sea level rise has nearly tripled compared with 1901–1971. The report indicates that human influence is very likely the main driver of the global retreat of glaciers since the 1990s and the decrease in Arctic sea ice.

As a heavily industrialized sector with a global impact, the oil and gas industry has a major role in tackling climate change. According to a report by McKinsey, the oil and gas sector must reduce its emissions by at least 3.4 gigatons of carbon-dioxide equivalent per year (GtCO₂e/yr) by 2050 compared to a business-as-usual approach.²

Initiatives such as the Oil and Gas Methane Partnership (OGMP) will play an important role in reaching these reduction targets. The OGMP is part of the Climate and Clean Air Coalition to Reduce Short-Lived Climate Pollutants (CCAC) initiative led by the UN Environment Program (UNEP), the European Commission (EC) and the Environmental Defense Fund (EDF). Sixty-two companies with assets on five continents, representing 30% of the world’s oil and gas production, have joined this partnership. The new OGMP 2.0 framework is now the gold-standard reporting framework that will improve the reporting accuracy and transparency of anthropogenic methane emissions in the oil and gas sector.

The need for measurement. For targets to be met, emissions must be measured and monitored. Continuous emissions monitoring systems (CEMS) are available to monitor a wide array of emissions. Available options range from standard systems for natural-gas-fired boilers to measure emissions such as carbon monoxide, carbon dioxide and nitrogen oxides to highly sophisticated, multi-component systems for waste-incineration plants measuring water soluble pollutants such as hydrogen fluoride, hydrogen chloride and ammonia.

The combination of environmental pressure, tightening regulations and a broader range of technology options is seeing a rising uptake of CEMS in industrial applications. The ARC Advisory Group forecasts a 4.8% growth in CEMS adoption between 2018–2023, with most of it being driven by Asia, as key players such as China, Southeast Asia and India increase their levels of

industrial activity.³ Growth is also expected to be generated by operators involved in electric power generation, incineration and chemicals manufacturing, which collectively represent the world’s largest markets for emissions monitoring systems.

Different types of CEMS. When it comes to CEMS solutions, users can select from a diverse choice of technologies that allow emissions to be accurately measured in a wide variety of refinery, petrochemical and chemicals applications. This includes the use in both production processes to measure gases and volatile organic compounds and for monitoring emissions from plants, such as from fired heaters, steam methane reformers and steam boilers. When it comes to measuring stack emissions, operators have a choice of techniques.

Extractive techniques. Commonly used for measuring gases, extractive techniques consist of two primary methods. Heated extraction involves extracting the sample gas from the stack by using a sample probe, heated line, gas conditioning equipment and a heated sample pump. Before analysis, condensate is usually removed from the sample and the temperature is reduced to protect the analyzers, commonly referred to as “cold/dry” measurement. The author’s company’s continuous gas analyzers^a work on this principle. As a modular gas analysis solution, it can combine up to four analyzer modules handling a total of six sample components. With ATEX 3G protection, the complete system can be designed without a purge, thus cutting maintenance time and costs, and increasing system availability by allowing maintenance operations or repairs at any time.

The alternative is to keep the gas hot all the way through the system, which is known as a “hot/wet” process. The sample must arrive at the analyzer inlet in a representative state that reflects conditions in the stack. The design of the sampling system must also protect against any sample loss or degradation. The author’s company provides an alternative Fourier-transform infrared spectroscopy (FTIR) solution^b to simultaneously measure multiple components. The system even allows the addition of further new components in the future by modifying the FTIR spectroscopy model.

In-situ measurement. In-situ “probe” analyzers are directly connected to the probe installed at the measurement point. Most in-situ systems use infrared measurement techniques.

Another popular technique is cross-duct analyzers. These analyzers project infrared (IR) or ultraviolet (UV) energy across the stack and detect the change in the energy state of the gas molecules as they absorb this energy at characteristic wavelengths.

Most cross-duct systems measure 1–2 gases over a range of wavelengths. Furthermore, as there is no contact with the target gases, they can require less maintenance and operator involvement. One drawback is that cross-duct systems can be more complicated to calibrate, although this can sometimes be overcome using an automatic calibration system.

The author's company's in-situ cross-duct analyzer^c for measuring gas component concentrations applies a highly selective, optical measuring principle of tuneable diode laser (TDL) absorption spectroscopy. The laser is selected for a single wavelength in the sample gas absorption spectrum, where no cross sensitivity from other gases occurs. The absorption line is scanned, and the receiver detects the absorption caused by the measuring component and calculates the gas concentration.

While in-situ analyzers can be installed directly on the stack with no sample handling, around 80%–90% of plants worldwide have a strong preference for extractive methods that tend to offer a lower cost of ownership.

In comparison to in-situ measurement, extracting a sample means only that the probe is in contact with the gas and not with any delicate optical components. After conditioning, a clean and dry sample is presented to the analyzer. The system can then be installed in an air-conditioned cabinet or shelter, protecting it against potentially harsh ambient conditions.

Whereas in-situ devices are usually limited to 1–2 components, multiple components can be measured simultaneously by using a sequence of sensors in an extractive system, requir-

ing fewer holes in the stack.

With the analyzer system usually installed at ground level in a clean and accessible environment, maintenance is much more convenient, components are easy to work on and test gas cylinders are available nearby to easily calibrate the devices.

A measured future. While addressing climate change is going to take a combined effort by governments, organizations and individuals worldwide, measurement systems are going to play a crucial role in helping the world to reduce emissions. As the value of these systems becomes more widely understood and the technologies become easier to implement, CEMSSs will certainly be set to play an increasingly central role in ensuring that all industries play their part in finding ways to limit their emissions. **HP**

NOTES

^a ABB's AO2000 and EL3000 continuous gas analyzers

^b ABB's ACFS000 FTIR analyzer

^c ABB LS25 analyzer

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Complete literature cited available online at www.HydrocarbonProcessing.com.



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Key considerations for the design and operation of a renewable diesel unit

Designs for the process configuration and operation of the unit are fundamental aspects in the production of renewable diesel. Renewable diesel feedstocks include vegetable oils, animal fats and used cooking oils.

A key advantage of the renewable diesel product is that it is fungible with conventional diesel and can be blended with no limitations.¹ However, the process for making renewable diesel has some specific challenges that differentiate it from traditional hydroprocessing. The feedstock contains impurities and introduces corrosion concerns not present with traditional crudes, and the hydrotreating chemistry produces side products that are atypical for conventional operations.

The severity of the operation also presents differences in heat release, hydrogen consumption and dewaxing requirements. Proper unit design and operation are key for producing a high yield of renewable diesel, while also addressing these challenges and enabling a safe and efficient operation.

Renewable feedstock contaminants. Renewable diesel feedstocks contain atypical contaminants, such as phospholipids and free fatty acids, as well as traditional contaminants like metals and chlorides.^{2,3}

Most of these contaminants must be removed via pretreatment steps before proceeding to hydroprocessing. Phospholipids consist of fatty acid chains, glycerol and a phosphate group, and have the tendency to polymerize at high temperatures, leading to fouling in both the feed preheat train and the hydrotreater. These compounds are removed via a process called

degumming, which solubilizes the phospholipids by using water, acid or enzymes.³

This process also removes metals—such as phosphorus, alkali metals and alkaline earth metals—that are associated with the phospholipid. Free fatty acids are those in which one of the chains on the triglyceride has broken off the propane backbone to form a carboxylic acid. These compounds also have the tendency to polymerize, but, beyond that, they contribute to acidification of the feed. A high concentration of free fatty acids increases the total acid number (TAN) and leads to corrosion of the feed delivery system. Once the renewable feedstock is mixed with hydrogen and is in the presence of the hydrotreating catalyst, these free fatty acids are hydrotreated and the concern is eliminated. The presence of metals—especially phosphorus—is a concern for active catalyst deactivation and reactor fouling, which leads to high pressure drop. Free fatty acids, metals and phosphorus are removed via chemical or physical refining processes and bleaching/adsorption steps.² Beyond the contaminants, certain feedstocks present unique challenges, such as the presence of polyethylene (PE) found in animal fats and used cooking oils.⁴

At high concentrations, PE can cause fouling and catalyst deactivation and must be removed along with the other contaminants. A renewable diesel producer has the option of purchasing previously pretreated feedstock or further investing in the producer's own pretreat system. While renewable feed pretreatment is outside the scope of the hydroprocessing unit, it is critical for maintaining the effectiveness of the hydroprocessing operation. Careful control and monitoring of

the contaminant levels enable operators to mitigate fouling and catalyst deactivation and to preserve cycle length.

Once the renewable feed is introduced to the hydroprocessing unit, the remaining mitigation is the inclusion of demetallation catalysts and grading materials to remove residual contaminants before they reach the active catalysts. Proper selection of demet and grading materials and their stacking arrangement, as well as control of the operating conditions to maximize metals uptake and minimize fouling, are key for protecting downstream catalyst.

Corrosion mitigation. Renewable feedstocks tend to decompose at high temperatures, increasing the concentration of free fatty acids and TAN.

A renewable diesel process must take into consideration the proper process configuration to ensure that the feed streams are sufficiently heated prior to the inlet of the hydroprocessing reactors, while avoiding high acidity that can lead to corrosion. This concern increases throughout the cycle length as reactor inlet temperatures rise, requiring more feed preheating. Appropriate materials selection for the metallurgy of the feed preheat section is critical for avoiding corrosion if high acid concentrations are encountered.

Once the feed has entered the hydrotreating reactors, the free fatty acids are reacted and are no longer a corrosion concern. However, hydrotreating renewable feedstocks results in the formation of carbon monoxide (CO) and carbon dioxide (CO₂), which can lead to the presence of carbonic acid. This could contribute to corrosion of equipment between the outlet of the hydrotreating reactors and sepa-

rator equipment, where the CO and CO₂ are removed from the system. The concentration of CO and CO₂ can be minimized through the appropriate design and operation of the hydrotreating section,^{5,6} and materials selection for this section of the unit can further mitigate potential corrosion. Additional corrosion concerns include the potential for chloride stress cracking and high-temperature hydrogen attack, although these are also of concern for conventional hydroprocessing units.

Heat release and hydrogen consumption. Hydroprocessing of renewable feedstocks generates higher heat release and consumes more hydrogen than traditional diesel processing. Renewable feedstocks from vegetable oils, animal fats and used cooking oils are made up of compounds known as triglycerides.^{5,6} These compounds have three fatty acid chains connected by a propane backbone. Different feedstocks have variations in both the length of the chains and the number of unsaturated bonds. In conventional hydrotreating, the desired chemistry is hydrodesulfurization, hydrodenitration and aromatic saturation. In the hydrotreating of renewable feedstocks, the desired reactions are saturation of the double bonds on the fatty acid chains and hydrodeoxygenation to produce n-paraffins, water and propane.^{5,6}

Both chemistries result in extremely high heat release and hydrogen consumption. Catalyst selection and design of the catalyst stacking arrangement, quench capabilities, liquid recycle and process controls are critical to ensuring safe operation of the unit, preventing runaway reactions,

and avoiding premature coking and deactivation of the catalyst.

Competing reactions to hydrodeoxygenation are decarbonylation, which produces CO and water as side products, and decarboxylation, which produces CO₂ as a side product. Both reactions lead to yield reduction, since carbon is lost as CO and CO₂, rather than retained on the paraffin chain. CO and CO₂ can react with hydrogen to form methane and water, generating additional heat that can lead to coking.

The catalyst selection and stacking arrangement, as well as process conditions (such as pressure and treat gas availability), impact the selectivity between hydrodeoxygenation, decarbonylation and decarboxylation and, therefore, are important for controlling the overall desired yield.

Temperature is another factor for selectivity, and, as the unit ages, the selectivity will shift for these three reactions. Hydrodeoxygenation maintains the highest yield of the carbon number of the feedstock; however, this reaction also consumes the highest amount of hydrogen (FIG. 1).^{5,6} Therefore, renewable diesel processes require high treat gas availability and high makeup rates to ensure that sufficient hydrogen is present for the desired dominant reaction.

Managing treat gas quality. CO, CO₂ and water generated during hydrotreating must be removed before the hydrotreated stream passes onto the dewaxing reactor to ensure high dewaxing yields. Proper design and operation of the separator equipment and gas treating system are needed to manage the concentration of these contaminants. Specifically, a purge stream

is needed to control the concentration of contaminants like CO, but it is important to minimize the flow of this stream to manage the purity of the treat gas and the required amount of makeup hydrogen.

Additionally, sulfur from dimethyl sulfide, hydrogen sulfide (H₂S) or another source is required to maintain the sulfide state of the hydrotreating catalyst. The gas treating system is responsible for balancing the level of H₂S to ensure that enough is present for the catalyst while avoiding it cycling up over time. Similarly, the gas treating and purge systems should remove sufficient concentrations of CO and CO₂ to ensure that these do not cycle up and lead to inhibition of hydrotreating catalyst activity.

Other components to consider are the concentration of propane, which is the backbone of the triglyceride molecules and which is generated during hydrotreating, and methane formed from methanation reactions. Although propane and methane will not inhibit catalyst activity, they can dilute the treat gas purity.

Cold flow improvement. Hydrode-waxing of renewable feedstocks is key for meeting cold flow properties. The composition of hydrotreated conventional diesel is a mixture of n-paraffins, aromatics and naphthenes—whereas, the composition of hydrotreated renewable diesel is mainly n-paraffins. N-paraffins have extremely poor cold flow properties, and must be either isomerized or cracked to meet diesel cold flow specifications.

For example, the cloud point of a conventional hydrotreated diesel may be approximately 5°C to -5°C, while the cloud point of a renewable hydrotreated diesel is typically closer to 25°C or higher. Therefore, to produce a -15°C diesel product, the conventional sample only requires 10°C–20°C of cloud point improvement, while the renewable sample requires 40°C of cloud point improvement. The higher dewaxing requirement is not a function of the design and operation of the hydrotreating section, but is rather due to the composition of the renewable feedstock. Although cracking reactions can improve cold flow properties, they can also lead to yield loss.

Therefore, isomerization chemistry, specifically that which adds multiple branches to the paraffin rather than a single branch, is preferred to maintain yield

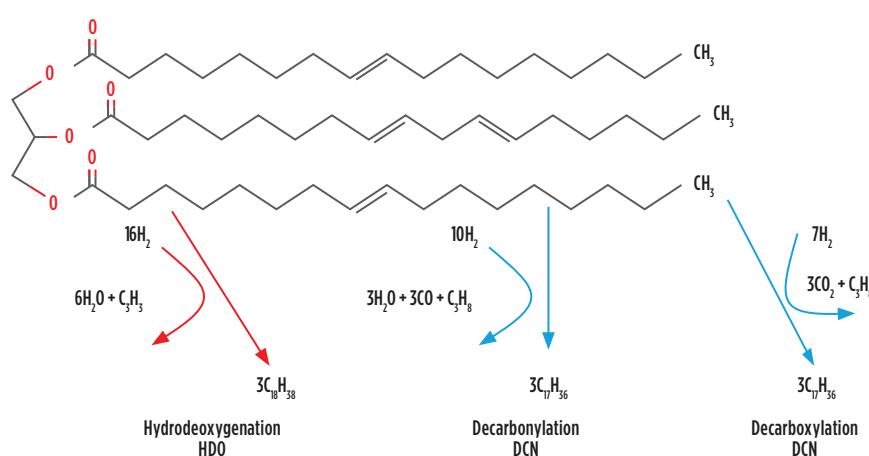


FIG. 1. Hydrodeoxygenation maintains the highest yield of the carbon number of the feedstock; however, this reaction also consumes the highest amount of hydrogen.

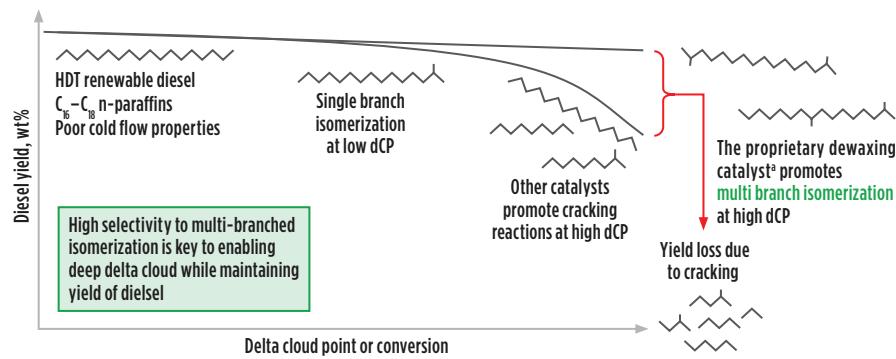


FIG. 2. The proprietary dewaxing catalyst^a can help promote multi-branch isomerization.

in the diesel boiling range. The higher the cloud point improvement, the more important it is to selectively isomerize vs. crack to maintain diesel yield.

The author's company's proprietary dewaxing catalyst^a is formulated to meet diesel cold flow specifications, even at deep delta cloud, while maintaining high liquid yields through its selectivity to multi-branch isomerization.⁷

Increasing interest in the production of jet fuel—or sustainable aviation fuel (SAF)—has the potential to shift the design and operation of renewable fuel processes. For co-production of diesel and jet fuel, this may require changes to the product separation equipment and operating severity, thereby introducing additional capital and operating expenses.

Renewable feedstocks typically have a narrow boiling range; therefore, the operating conditions need to drive molecules from the diesel boiling range to the jet fuel boiling range. The goal is to make this transition with the highest jet fuel and diesel total yield, while avoiding the production of naphtha and light ends. The proprietary dewaxing catalyst^a can help manage this balance (**FIG. 2**).

Takeaway. Production of renewable diesel includes technical challenges (including the removal of contaminants, corrosion concerns and metallurgy selection, as well as the management of high heat release and hydrogen consumption) beyond those of conventional processing, thus preventing catalyst activity inhibition and providing deep dewaxing, while maintaining high liquid yields. The design of the process configuration and operation of the unit are critical for the mitigation and management of these factors. The author's company's proprietary renewable

diesel process^b features a two-stage unit design that uses the proprietary dewaxing catalyst^a and processes a range of renewable feedstocks to produce high yields of renewable diesel, with the flexibility to also produce nominal volumes of jet fuel. The use of two stages enables separate control of the hydrotreating and dewaxing chemistries, thus allowing refiners to better adjust to changing objectives compared to single-stage processes. The author's company's expertise as both an owner and operator of hydroprocessing units allows it to address all the key challenges noted in this article in the design and operation of the proprietary renewable diesel process and to deliver a high-performance technology that meets renewable product objectives. **HP**

NOTES

^a ExxonMobil's Bio-Isomerization Dewaxing (BIDW™) catalyst
^b ExxonMobil Renewable Diesel (EMRD™) process

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Comparing green fuels for marine engines—Part 1

The marine shipping industry, which accounts for 80% of global trade and 3% of annual global carbon emissions,¹ must adhere to stringent International Maritime Organization (IMO) goals of reducing total annual greenhouse gas (GHG) emissions by at least 50% below 2008 levels by 2050.² Essentially, GHGs—in the form of carbon dioxide (CO₂) emissions—must be reduced by 40% by 2030 and by 70% by 2050 to achieve this goal. Similarly, the European Union (EU) plans to reduce its annual CO₂ emissions to 40% below 2005 levels by 2050.³ To achieve these reductions, marine fuels must produce near-zero emissions at every step of their lifecycles.

Large oil companies have been pressured to undertake the GHG emissions footprint reduction. Part of this push is to make green fuels with inherently lower GHG emissions than conventional fossil fuels. The U.S. Environmental Protection Agency (EPA) defines alternative fuels to include gaseous fuels (such as hydrogen, natural gas and propane), alcohols (such as ethanol, methanol and butanol), vegetable and waste-derived oils, and electricity.⁴ Of these alternative fuels, LNG, hydrogen, ammonia, methanol and biofuels are considered potential green fuels for the marine industry. These alternative fuels must not only reduce emissions, but must also be transportable, storable, producible and inexpensive, and able to generate enough energy to propel large ships across the world.

However, the shipping industry primarily uses hydrocarbons—in the form of heavy fuel oil (HFO) and marine gasoil (MGO)—in its engines because they are cost effective and widely available. To adhere to emissions reductions by 2050, the Institute of Electrical and Electronics Engineers (IEEE) forecasts that at least 50%

of all marine engines will run on green fuels by the mid-2040s (FIG. 1).

Significant efforts are required to innovate pathways to use green fuels in existing or new engines and in bunkering/port infrastructures. As an initial step, an assessment of the technical performance and environmental impacts of each future green fuel is required. Multiple factors such as cost, availability, production and infrastructure vary for these fuels and may influence the feasibility of their use. A thorough investigation of these potential fuels is needed to evaluate the practicality and feasibility of each option. Do these green fuels actually reduce GHG emissions? Will they operate with the same

throughput as fossil fuels? How much will they cost to implement? For green fuels to be attractive to both shipowners and fuel producers, they must correlate to the functionality of fossil fuels and not just meet the emissions requirements.

Finally, standardized engineering definitions and calculations are needed to be able to make comparisons on an equal basis, such as the use of standardized emissions lifecycle models to calculate carbon footprints.

Green fuels for marine engines. This article examines five potential green fuels for marine engines: LNG, hydrogen, ammonia, methanol and biofuels.

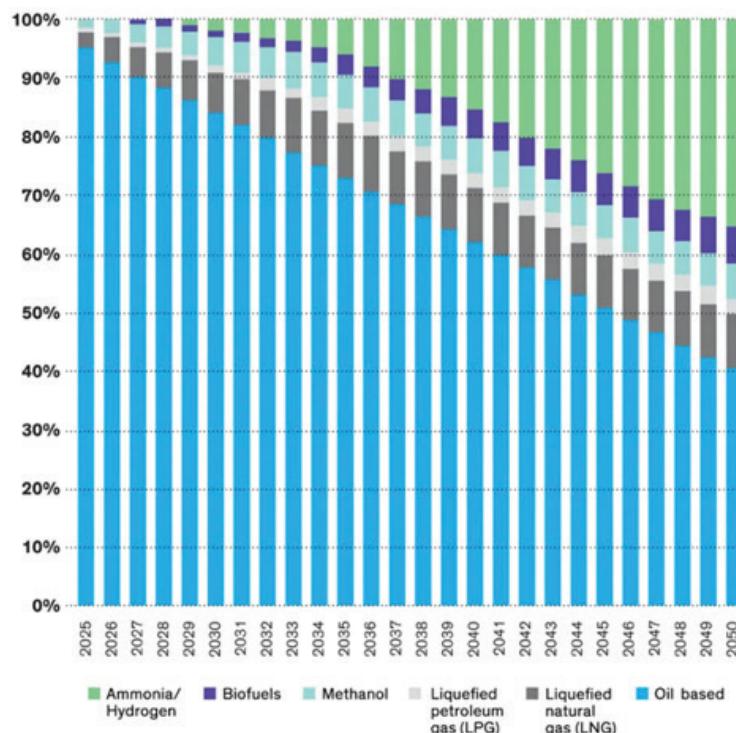


FIG. 1. Forecast of fuel usage in the marine industry. Source: IEEE.

LNG. LNG is leading the race as a substitute green fuel. It has a relatively high energy density of 22.2 MJ/L, a rapidly developing infrastructure and is widely available. However, it is viewed as a non-sustainable transition fuel since it emits 2% more carbon during its lifecycle. LNG has the potential to be a bridge fuel to hydrogen due to similar cryogenic storage requirements.

Hydrogen. Hydrogen is an energy-dense fuel (FIG. 2) and can be produced with no GHG emissions. With an energy density of 8.5 MJ/L, liquid hydrogen can be used in both internal combustion engines (ICEs) and fuel cells. However, the journey using hydrogen sustainably is long winded. At present, gray hydrogen is produced via methane reforming, which emits GHGs comparable to HFOs. Zero-carbon-emissions hydrogen is produced from renewable-electricity-driven water electrolysis, which is more expensive than gray hydrogen production. Although hydrogen-energy dense, it has a much lower energy density vs. fossil fuels, which will result in cargo capacity limitations.

Ammonia. With an energy density of 11.5 MJ/L, liquid ammonia is another viable option that can be used in existing engines and bunkering facilities. Used either as a hydrogen carrier or as a fuel, green ammonia can have zero emissions within its lifecycle when produced with green hydrogen or directly via electrochemical cells. However, just like hydrogen, ammonia is less energy dense than conventional fossil fuels. It is also highly

toxic and requires strict guidelines.

Methanol. Methanol has a high energy density of 16 MJ/L. It gained popularity due to its availability and easy storability. Renewable methanol (i.e., bio-methanol or e-methanol) has the potential of reducing GHG emissions by 65%–95%. However, it is less dense than traditional fuels, and renewable methods are significantly more expensive than conventional fossil-fuel-derived methanol.

Biofuels. Biofuels are the most researched alternative fuel. Several marine engines and fueling infrastructures are compatible with biofuels, with minimum modifications. Bio-derived fuels (e.g., biodiesel) show potential. The major challenge with the use of biofuels in the marine industry is the significant increase in production required to satisfy demand, which will necessitate more land reuse and the elimination of vegetation. The sustainability of biofuels is put into question when the lifecycle analysis and carbon offset are considered. GHG emissions reductions are hindered by land-use changes and other upstream emissions.

These green fuels have the potential to reduce carbon emissions. However, when the exact quantities are presented alongside the lifecycle analysis, their viability is questioned. The primary challenges are that green fuels have lower energy densities vs. conventional fossil fuels. There are also diverse issues regarding availability, port and bunker infrastructure, engine development challenges, cost, supply and safety.

The lifecycle emissions further highlight the misconception that people have about green fuels and their emissions reductions.

As a possible solution, a multistage strategy must be developed. Since infrastructure exists for LNG, biofuels and conventional methanol, these fuels can be viable as short-term solutions (5 yr–10 yr). Corporations should start moving away from LNG, gray methanol and biofuels in the medium term (10 yr–15 yr) and begin focusing on converting LNG engines/facilities to use green hydrogen fuel and converting biofuels/methanol to e-methanol. As a long-term solution (15 yr–20 yr), corporations should invest in advancing green ammonia technology. Since ammonia infrastructure already exists and can be used in existing engines/bunkering facilities, green ammonia has the capability to be used as a sustainable fuel for the marine industry, while also ensuring zero GHG emissions. It would also be beneficial for diverse fuel alternatives to continue being used to provide flexibility to the industry. Therefore, in the long term, most ships should be fueled by ammonia, while smaller ships can be fueled by hydrogen and existing methanol ships should continue operations using e-methanol.

Statement of the problem. The questions that the marine industry are battling with is which green fuel is the most feasible alternative for short-term and long-term sustainability, and is it realistic? This article provides a review analyzing the feasibility and practicality of several green fuels. First, it is important to consider the source/feedstock and production mechanism used to produce the fuel—the amount of energy required to produce the fuel and the relative cost of production. Then, the practicality of each fuel is investigated based on the port and bunker infrastructure required, fuel engine development, projection of the correlation between fossil fuels, the fuel's suitability among long-range vessels, supply issues and the associated risks involved. The short-term and long-term initiatives associated with each green fuel are analyzed through an assessment of current and projected technological projects, research and development initiatives and projects, and competing industries. Finally, the overall feasibility outlining the benefits of each fuel and the lifecycle analysis of GHG reduction of each fuel are provided as recommendations.

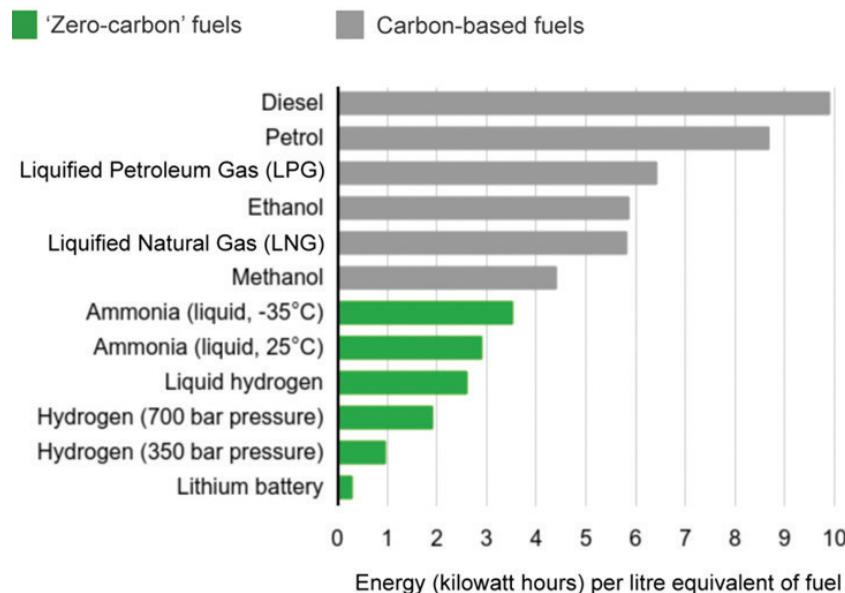


FIG. 2. Energy density of fuels per liter equivalent of fuel. Source: The Royal Society.

Part 1 of this article will examine LNG, hydrogen and ammonia. Part 2, to be published in the February issue, will examine methanol and biofuels.

RESULTS AND FINDINGS

The following are the results and findings for LNG, hydrogen and ammonia.

LNG. As a preliminary requirement, an alternative marine fuel should contain less carbon than the existing hydrocarbons used in the industry. LNG is considered an interim potential solution, since it contains less carbon per unit of energy.⁵ When burned during combustion, LNG will release less CO₂ vs. conventional fuels. For years, LNG has been used as a secondary fuel through combusting boil-off gas from LNG cargoes.⁶ Due to the IMO's sulfur standard regulations, LNG could act as a fuel replacement. Many companies in the marine industry considered switching to LNG-fueled engines, since they emit less than 0.1% of the fuel-equivalent threshold.⁷

LNG is produced via the hydraulic fracturing extraction of natural gas, which is then liquefied and stored under cryogenic conditions (-160°C). The main source of natural gas is primarily underground reserves, but some companies utilize biogas. Natural gas in its liquid state is about 600 times smaller in volume than in its gaseous state.⁸ Therefore, natural gas is liquefied to enable easy global transportation.

In terms of energy requirement, the production process extraction and liquification is energy intensive. It requires a relatively high initial capital investment, which involves exploration, drilling, piping to a coastal liquification plant and the liquification process. In addition, shipowners can expect to pay approximately \$5 MM more for an LNG-fueled vessel than one that is run off conventional marine fuels.⁹ LNG engines require a larger investment than installing scrubbers on ship, which is another alternative solution to adhere to the IMO requirement. However, an offset of the capital investment is expected, due to fuel cost advantages—LNG is the most cost-efficient fossil fuel, once its production infrastructure is secure.¹⁰

However, LNG has a lower energy density than diesel. The Alternative Fuels Data Center reports that LNG has a specific energy density of 21,240 Btu/lb and a mass density of 3.49 lb/gal, while low-

sulfur diesel has a specific energy density of 18,122 Btu/lb and a mass density of 7.09 lb/gal.¹¹ While the specific energy density is slightly comparable, the large difference in mass densities means that diesel has nearly twice the amount of energy/gal when compared to LNG. Ships fueled by LNG also require more space for fuel tanks, which may limit cargo capacity.

All major shipping companies are either developing, or have already launched, a variety of engines that run on LNG. These technologies include a two-stroke engine and a dual-fuel, slow-speed engine that operates on LNG as the primary fuel and on diesel as a secondary fuel.¹² A variety of engines can use LNG or natural gas. These include steam engines, lean-burn spark-ignition engines, low-pressure injection dual-fuel (LPDF) engines, high-pressure injection dual-fuel (HPDF) engines and gas turbines.

Although LNG emits 20%–30% less carbon during combustion, LNG has a large carbon footprint. Pavlenko *et al.* analyzed LNG's lifecycle when used in different engines.¹³ Since LNG is mostly methane, each engine releases unburned methane due to incomplete combustion. Fugitive methane is a more potent GHG than CO₂, and its emissions are more detrimental to the environment. To perform a complete lifecycle analysis, the upstream and downstream emissions had to be evaluated. Pavlenko *et al.* evaluated the upstream emissions of LNG using GHS, regulated emissions and energy use in transportation (GREET) modeled by

the Argonne National Laboratory. Downstream emissions were sourced from available company data sets. As shown in FIG. 3, LNG has higher upstream emissions than conventional fuels such as MGO, very-low-sulfur fuel oil (VLSFO) and HFO. These high emissions are a result of high methane emissions due to leakage that occurs during extraction, processing and transport. In addition, the liquification process contributes to upstream emissions. Although LNG has lower downstream emissions than conventional fuels, LNG has a higher total GHG emissions rate when the upstream emissions and methane slips are accounted for, irrespective of engine types.

Hydrogen. According to the International Energy Agency (IEA), hydrogen is a potential carbon-zero fuel alternative. With byproducts like water and steam, hydrogen can eliminate pollutants from the transportation industry. Hydrogen is also abundant in the environment and can be produced from diverse sources. Its use in the transportation sector is still in the primary phase. Hydrogen became popular with the use of fuel-cell-powered vehicles. Using hydrogen fuel cells integrated with an electric motor is about three times more efficient than gasoline-powered ICEs.¹⁴ Hydrogen is used in light-duty, fuel-cell vehicles; however, can it be used to propel ships across the ocean?

One challenge with using hydrogen as a fuel is its production process. Readily available substances, such as organic matter, water and hydrocarbons, can be used

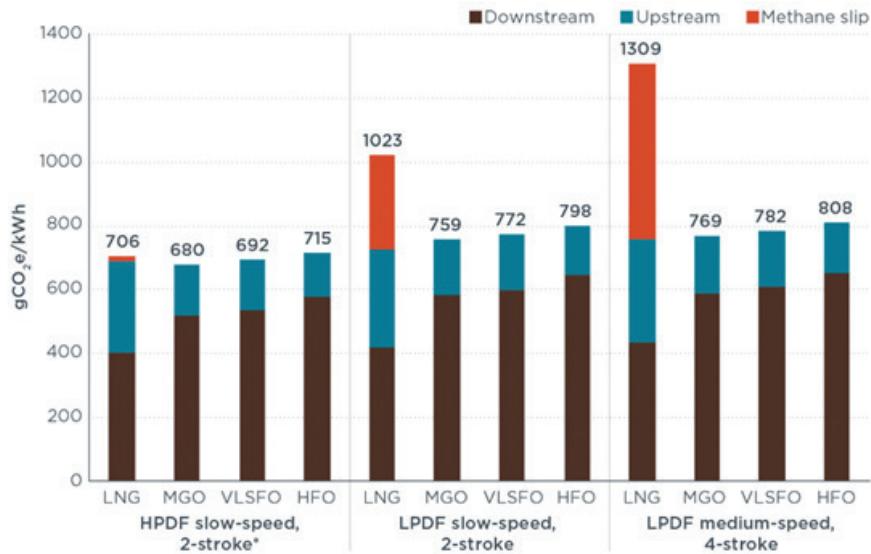


FIG. 3. Lifecycle GHG emissions by engine and fuel type.⁵

as a source of hydrogen.¹⁴ FIG. 4 depicts the relevant sources of hydrogen and their associated names. The most common source of hydrogen is methane/natural gas, which is called gray hydrogen. Steam methane reforming is used to convert methane to hydrogen through the process of synthesis gas generation, hydrogen generation and gas purification. CO₂ is the primary dilutant removed during the purification process. Similarly, brown hydrogen is hydrogen that is produced from coal, using the same steam methane reforming (SMR) process.

Although SMR is the cheapest way to produce hydrogen, this process emits a significant amount of carbon, resulting in emitting CO₂ as a byproduct.¹⁵ SMR emits about 10 t of CO₂/t of natural gas, while coal produces 19 t of CO₂/t of coal.¹⁶ To minimize the emissions associated with brown hydrogen, carbon capture technologies are added to the SMR purification step to create blue hydrogen. However, this process relies on fossil fuel sources, which still have a carbon footprint. Hydrogen produced via water electrolysis has the potential to eliminate emissions from this production step. Water electrolysis uses electricity to separate hydrogen and oxygen from water. Electrolysis powered by fossil-fuel-sourced grid electricity is called blue hydrogen, while electrolysis powered by renewable energy is referred to as green hydrogen. While green hydrogen is the most environmentally friendly way of producing hydrogen, it is the most expensive option. Another production option—turquoise hydrogen—is still in the research phase. Turquoise hydrogen is

produced through the process of pyrolysis, which converts methane to pure solid carbon and hydrogen.

For hydrogen to be a reasonable fuel alternative, green hydrogen should be the primary type used in engines or fuel cells. Significant investments are required in renewable energy technology. At present, only 3.9% of the hydrogen produced comes from water electrolysis.¹⁵ Intervention is needed to reduce the cost of green hydrogen, so that it may be used as a fuel. Fortunately, the cost of green hydrogen has reduced by approximately 50% since 2015 and is forecast to continue to decrease as more projects focus on renewable energy.¹⁶ Hydrogen production will also need to increase significantly to meet the demands of the marine industry. Most produced hydrogen is used as a component in the chemical industry and in oil refineries.

Like LNG, hydrogen has a lower energy density than conventional marine fuels. Hydrogen has an energy density of 8.5 MJ/L, which is about 15% less than the energy density of diesel.^{16,17} Therefore, ship capacity becomes a significant disadvantage for hydrogen's use in the marine industry. To store the same amount of cargo on board will require fuel tanks to be seven times larger than diesel tanks.¹⁶ Hydrogen could be ideal for smaller ships or for shorter trips that have frequent access to bunkering stations. Larger ships would need hydrogen storage that takes up less space on the ship (e.g., ammonia or liquid hydrogen).

Hydrogen must also be stored at high cryogenic conditions (-253°C), requiring expensive bunkering facility requirements

and stringent safety procedures. According to the IEA, the cost infrastructure is offset by the cost of fuel when calculated at a 15 yr–20 yr lifespan.¹⁷ Once the fuel cost becomes competitive, hydrogen may be a viable fuel alternative in the future.

Hydrogen can be used directly as a fuel in an ICE and in fuel cells to generate electricity. Dual-fuel ICEs are a possible route for hydrogen; whereby, MGO can be used when the hydrogen inventory on ships runs out.¹⁵ However, there is presently no hydrogen fuel engine commercially available. There are also no federal regulations for design considerations for the use of hydrogen as a marine fuel, and, therefore, there is no formal approval for its commercial use. The U.S. Coast Guard may approve alternative design proposals for companies on a case-by-case basis.¹⁸ The knowledge gained from the use of LNG may bridge to developing design solutions for hydrogen-fueled vessels. Overall, there are many projects geared toward developing hydrogen technologies. For example, the U.S. Department of Energy (DOE) has funded many projects that focus on overcoming hydrogen's shortfalls.

Hydrogen's lifecycle analysis as a fuel is dependent on the source of production. Hydrogen production emits 60 MMtpy of CO₂, primarily from brown/gray hydrogen production, according to the U.S. EPA. Brown/gray hydrogen and HFO emit roughly the same amount of carbon.¹⁶ Like LNG, gray hydrogen has high upstream emissions that results from the extraction of natural gas. This includes methane leakage during the extraction process, along with methane slips during transportation and SMR processes. Blue hydrogen captures approximately 90% of the CO₂ emitted during the SMR process.¹⁹ However, this option still involves major upstream emissions. Howarth *et al.* conducted a study on blue hydrogen and found that it emits 9%–25% less CO₂ than gray hydrogen. However, since methane is used to power carbon capture technology, fugitive methane emissions are much greater than gray hydrogen. Howarth *et al.* concluded that the lifecycle GHG emissions of blue hydrogen are 20% times greater than with burning natural gas or coal. Turquoise hydrogen is still being researched, but it has the potential of minimizing carbon emissions from the hydrogen fuel lifecycle. The process produces solid carbon instead of CO₂, which eliminates the need for car-

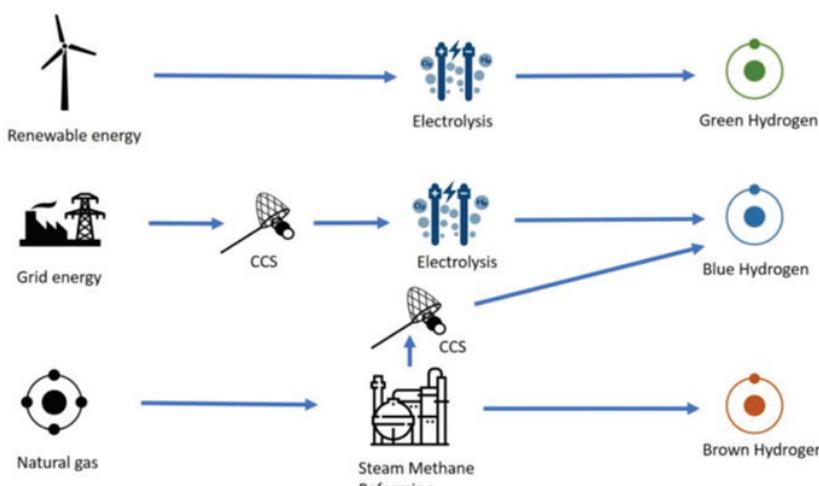


FIG. 4. The different types of hydrogen production.¹⁵

bon capture. The solid carbon can be used for other applications. However, methane is used as the feedstock and produces significant upstream emissions. These emissions can be reduced by using renewable energy to drive pyrolysis.²⁰ Green hydrogen is the optimal solution, since it does not produce emissions during production or combustion. However, emissions associated with renewable electricity production are not considered.

Ammonia. While some may think of ammonia as a hydrogen storage medium, ammonia can be used as a fuel in marine engines. In recent years, ammonia received a lot of attention as a potential future carbon-zero alternative fuel for the transportation industry. For example, Kang and Holbrook evaluated the feasibility of using ammonia as a fuel in light-duty cars.²¹ Marine shipping companies are also investing in ammonia-fueled vessels and engines.

Ammonia is a beneficial fuel alternative, since combustion produces only nitrogen and water. It is already shipped globally in huge quantities for the fertilizer industry. Ammonia is a liquid at room temperature and at moderate pressures, meaning it is relatively easy to store, and, despite common misconceptions, ammonia can be relatively safe to use.

Anhydrous ammonia is primarily produced from nitrogen and hydrogen via the Haber-Bosch process. There are different types of ammonia: gray/brown, blue, turquoise and green. The lifecycle emissions and prices are also dependent on the hydrogen production. Nitrogen is separated from air, using a low-energy technology. Additional research is being conducted on novel ways to produce ammonia. Biological nitrogen fixation is a potential source for green ammonia. It uses the nitrogenase enzyme to catalytically convert atmospheric nitrogen to anhydrous ammonia.²² Electrochemical cells can also be used to convert water and nitrogen to green ammonia, which can eliminate the need for a separate hydrogen production step. Renewable energy may be used in this process to ensure zero carbon emissions.

With a density of 11.5 MJ/L, ammonia is twice as dense as hydrogen and more dense than liquid hydrogen.²¹ However, ammonia is less dense than diesel and requires less fuel tank capacity than hydrogen. Since ammonia is a liquid fuel at room temperature and has similar properties to

propane, it can be used in existing bunkering facilities. Minor changes to materials on vessels would be needed to ensure safety on board. Material compatibility requirements for shipping ammonia are well known and can be easily implemented at bunkering facilities and on marine vessels.

Regarding ammonia supplies, global ammonia production would have to significantly increase to meet global fuel demand. All the raw materials are readily available in the environment to meet the demand; however, large amounts of electricity will be required.²³ More bunkering facilities must be built to accommodate the increased production.

The associated risk with using ammonia is its toxic and corrosive nature. While ammonia is a toxic chemical requiring strict safety precautions, it is less flammable than hydrogen and LNG. It has the potential to emit nitrous oxide, which can be eliminated with the use of a catalyst to favor the reaction that produces atmospheric nitrogen and water as combustion products.

Corporations are in a race to develop different engines to facilitate the use of ammonia as a fuel. These technologies include two-stroke and four-stroke ammonia engines, as well as ammonia fuel cells that will convert ammonia to hydrogen to produce electricity. One major shortfall of ammonia is its inability to ignite quickly. Secondary fuels, such as hydrogen or conventional fuels, could solve this issue in a dual-fuel ICE. Another solution is to develop a spark-ignited gas engine to facilitate the combustion of ammonia.

Part 2. Part 2 will be published in the February issue. **HP**

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HP | Carbon Capture/ CO₂ Mitigation

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Tips to avoid pitfalls in CO₂ capture projects

In recent years, growing concern about increasing atmospheric carbon dioxide (CO₂) levels has put mounting pressure on governments and on processing industries to curb carbon emissions. Consequently, this has accelerated CO₂ capture projects. However, an array of challenges that could, if not addressed adequately, hamper these otherwise well-intentioned projects. This article examines the pitfalls that a risk manager should consider to eliminate or minimize risks to ensure safety, environmental sustainability and economic success.

CO₂ mitigation/elimination technologies adoption. Many companies/organizations in the global hydrocarbon processing industry are investing in new technologies and processes to mitigate or eliminate CO₂ emissions. However, differences among science communities and industry exist in how quickly this transition should take place. Atmospheric experts stress the need for rapid transition, while industry professionals urge a calibrated and gradual approach. On a national level, a rapid transition to less-familiar technologies or nascent low-carbon or zero-carbon technologies could cause massive economic and societal disruptions. Some experts maintain that lofty phrases such as "carbon capture," "zero-carbon economy" and "carbon-free world" tend to fuel hype while presenting a consequent lack of adequate thought to the risks associated with these relatively less-familiar technologies. However, astute risk managers recognize the need to do both: making quick transitions coupled with pragmatic risk minimization.

The scope of curtailing and/or managing atmospheric CO₂ levels is vast and includes the direct capture of CO₂ from

atmosphere, along with planting trees, shifting to non-fossil fuel technologies, and capturing CO₂ from flue gas, among others. Flue gas CO₂ emissions are a significant portion of emissions. This article focuses on the processes and projects to capture CO₂ from flue gases.

Post-combustion CO₂ management involves the removal of CO₂ from flue gas, compression, liquefaction, storage and reuse, where practicable. Several approaches exist for removing/concentrating CO₂ from flue gas (e.g., absorption, adsorption, permeable membranes and cryogenic separation). As shown in FIGS. 1 and 2, absorption and adsorption technologies have gained wide industrial acceptance.

Absorption technologies use organic amines such as monoethanolamine (MEA) and its blends. Starting from MEA absorption, technologies have improved to minimize several weaknesses of the MEA process, including oxidation of the solvent, corrosivity and intense energy requirements. In recent years, technologies have focused on adsorption-based routes, where CO₂ from flue gases are adsorbed on solid sorbents (e.g., activated carbon, zeolites and others). These processes include fixed beds with solid sorbents, which undergo adsorption followed by thermal desorption. Although the adsorption-based technologies avoid the disposal challenges of liquid solvents, they still must contend with the eventual disposal of solid sorbents. A fluid-bed catalyst process is also being offered by a technology licensor, promising lower capital and operating costs. Unsurprisingly, each process has its benefits and risks. In addition to the risks of the carbon capture process from flue gases, transporting CO₂ and storage risks merit careful consideration, as well.

PITFALLS TO AVOID

The following are six pitfalls to avoid when developing CO₂ capture projects.

Considering CO₂ capture in isolation. Hastily formulated CO₂ capture projects could result in missing other strategically important segments, including CO₂ transport, long-term storage and the potential reuse/recycle of CO₂. Depending on a plant's location, infrastructure to transport CO₂ to storage caverns could involve a significant investment, along with financial and environmental risks. In the long term, massive investments are needed in pipeline and storage infrastructure. Tank and rail transport—though a viable option for relatively small quantities—quickly become uneconomical for large-scale transports. Each mode of transportation also has potential risks. Several major issues to consider include:

- Permitting and right-of-way considerations:** Permitting for CO₂ pipelines involves detailed application preparation, design reviews, emergency response plans and public reviews. Establishing good public rapport will help expedite the permit approval process. Transporting CO₂ by ship and/or subsea pipelines must comply with several international codes and regulations and would require environmental risk assessment—akin to those performed for National Environmental Policy Act (NEPA) projects. Unsurprisingly, this is a very rigorous and time-consuming process. For inland pipelines, determining a suitable route requires geo-tech work, including soil conditions, topography, climate

- variations and areas with heavy population density, among others.
- Corrosion:** Although liquefied CO₂ does not present a flammability hazard and dry CO₂ does not present a corrosion hazard for ordinary carbon steel, prudent pipeline designs should include monitoring and safeguards against impurities such as sulfur, mercaptans or hydrogen sulfide (H₂S), water and others, depending on the stack gas composition. One key safeguard may include upgrading to austenitic 316 stainless steel, as low-alloy carbon steel corrosion could be a problem.
 - Monitoring and specification requirements:** In addition to monitoring for corrosion, online instrument/control systems should be provided to ensure that product specifications adhere to parameters set for storage in caverns. For example, instrumentation could include online analyzers for water, sulfur and impurities, hydrocarbons and oxygen—and flowmeters/meter provers and interlocks can help halt flows to storage caverns in the event of off-spec CO₂.
 - Tank car and truck/marine transport:** These types of transportation entail significant handling risks of asphyxiation and thermal shock. Tank cars or truck transports tend to involve considerable handling risk. Loading/unloading racks should include automatic programmable logic controller (PLC) sequenced operations or some other means to minimize human interaction. In addition, loading/unloading stations should have ample ventilation to minimize the asphyxiation hazard.
 - Transport disruptions:** Risk analyses must consider potential disruptions and safety mishaps (e.g., ship collision and/or fire, truck/train accidents) and should provide adequate warning systems and safeguards to minimize mishaps. The potential of asphyxiation for workers in ships also merits consideration. In the event of a subsea pipeline rupture,

cryogenic CO₂ will be released and could affect (carbonic acid and the resulting low pH) marine life. However, unlike hydrocarbon spills, CO₂ will escape. Depending on the magnitude of the leak, the CO₂ vapor cloud could pose an asphyxiation hazard for ships/vessels in the vicinity.

- Reuse and recycle:** Reuse and recycling are key pillars of a sustainable/circular economy. The reuse of CO₂ for enhanced oil recovery (EOR) or in the cement industry can help improve project economics. However, in the long term, EOR might be impacted by stricter government regulations. Fortunately, considerable work is in progress to develop new avenues for the reuse and recycling of CO₂.

Technology selection. Obviously, a technology that does not meet safety, productivity and environmental goals would ruin an investment, as well as tarnish a company's public image. Companies must take a systems approach in selecting technology that matches the organization's existing process. The following are several pitfalls to consider:

- Equipment sizes for the CO₂ absorption technology:** Liquid solvent-based technologies could entail large equipment and solvent flowrates—hence, larger real estate. A congested layout would make it difficult to accommodate new equipment additions and structural foundation requirements. In addition, utility requirements (e.g., steam consumption, power requirements, nitrogen and instrument air) must be accounted for. CO₂ capture processes tend to be steep in capital and operational expenses.
- Maturity and reliability of the technology:** Nascent technologies lack long-term reliability data. Conversely, technology that is "too mature" could face obsolescence problems. For example, amine-solvent-based processes are relatively mature in comparison with recent membrane processes, which have less environmental impact but lack operational history. It is a delicate balancing act between reliability and obsolescence.
- Liquid solvent or solid adsorbent disposal issues:** Even in disposal,

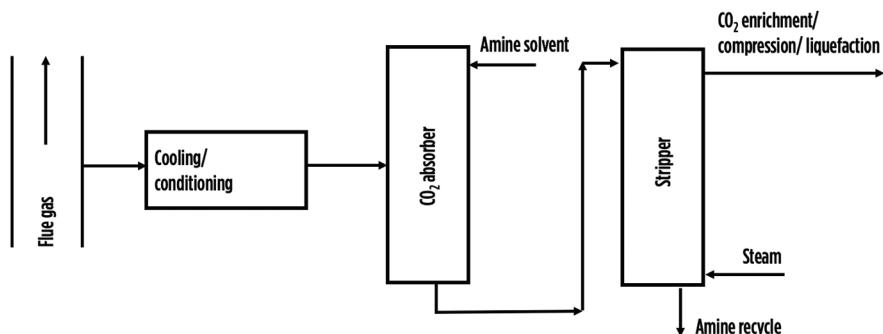


FIG. 1. Amine-based CO₂ absorption process schematic.

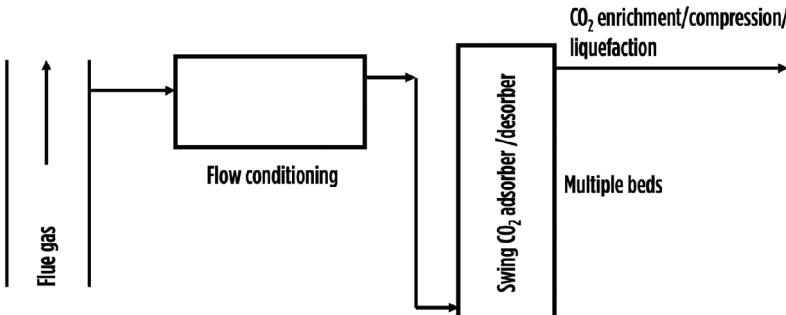


FIG. 2. Adsorption-based CO₂ recovery from flue gas.

one must consider the potential adverse environmental effects resulting from the disposal process.

concerns and other issues). Resultant litigation and delays could render the project

Improving operations to minimize CO₂ formation. Furnace or boiler operations at high levels of excess air will increase flows through the CO₂ capture process and lead to suboptimal operations, while scant excess air could cause unsafe conditions. Optimizing the operation of upstream equipment will improve CO₂ capture and enhance overall productivity. In addition, switching to fuels that generate lower amounts

of CO₂/Btu (the amount of CO₂ produced per Btu of heat release) will help lower the size of the CO₂ capture equipment. For example, the amount of CO₂ released per MMBtu of heat output for natural gas is approximately 40%–50% lower than that generated by fuel oils, such as diesel. However, this option may not be viable for brownfield projects.

Numerous approaches are available for amine disposal, including physical (membrane), chemical or biological treatments. Each of these processes have benefits and challenges. Regardless, the goal is to minimize the overall environmental impact.

- **Liquid or solid sorbent sensitivity to chemical species in the flue gas, such as oxygen, nitrogen oxides (NO_x) and sulfur compounds:** For example, some sorbents may be too sensitive to sulfur or sulfur derivatives and may require sulfur removal in the flow conditioning step (**FIGS. 1** and **2**). This will add to the project's cost. In addition, particulates from flue gas could cause plugging problems, operational challenges and low productivity.
- **Amine emissions could pose multi-phase environmental issues:** Amine emissions can affect air quality and cause water pollution (as rainwater will dissolve amines), which can lead to soil contamination problems. Similarly, environmental systems must be robust enough to handle amine and byproduct spills.
- **Acceptance from communities:** Despite well-intended efforts to improve the environment, CO₂ capture projects can receive a tepid response or even fierce resistance and/or legal challenges from nearby communities if their concerns are not addressed adequately (such as regarding noise levels and traffic during construction, long-term noise levels, amine emissions, odor

unsustainable and could generate—in the short term—public concern or distrust about a company's environmental stewardship.

- **Operational upsets:** In the event of an operational upset that results in unburnt hydrocarbons in flue gas, the CO₂ capture plant could spread a flammability hazard over a wide area. Control philosophies should address this hazard, along with similar plant upset issues.
- **Flue gas CO₂ concentrations and effective absorption:** Depending on the source, CO₂ concentrations in flue gas vary. For example, gas turbine flue gases typically contain 3 vol%–4 vol% CO₂. Flue gas in gas-fired heaters or boilers has CO₂ levels of 8 vol%–10 vol%, and fuel-oil-fired boilers have even higher CO₂ levels. Low concentrations of CO₂ mean a lower driving force for absorption and may require higher concentrations of amine. Plants must establish an operating window for CO₂ concentrations.
- **System integration:** Although instrument and control system vendors have made significant efforts to interoperability, at the plant level, personnel must spend a considerable amount of time and resources to ensure smooth operations. For example, if the distributed control system (DCS) is provided by X and the CO₂ capture vendor has its system based on DCS Y, then data protocols must be addressed carefully. Inadequate consideration of DCS alignment will cause recurring data-management issues, along with operational and safety problems.

Long-term considerations. The CO₂ capture plant/project lifespan may be 25 yr–30 yr; therefore, it requires some thought on several broad issues. Some of the issues may not be easily manageable or even amenable to quantitative analysis; nonetheless, decisions must be made in the face of volatile information. Several of these issues include:

- **Supply chain robustness and CO₂ markets:** As with any project or plant operations, supply chain reliability is crucial. Similarly, demand for CO₂ will impact operating rates and emissions.
- **Stability of disposal contractors:** Implicit requirements of solid waste disposal and Resource Conservation and Recovery Act (RCRA) regulations include an assessment of a waste disposal contractor's financial stability; the same will apply for waste disposal from CO₂ capture projects.
- **Environmentally advanced technology suppliers:** The move toward environmentally responsible processes and technologies will continue. In selecting any technology, one should identify segments that are problematic from an environmental sustainability view, such as high solvent or adsorbent

consumption that requires proper disposal. Other aspects to consider are high energy requirements and systems with lower reliability. After these problematic systems are identified, a strategy should be put into place to gradually move away from these systems. History shows that technologies with large environmental footprints tend to become extinct and get replaced with environmentally savvy technologies. CO₂ technologies should be able to facilitate environmental upgrades without a massive infusion of investment.

Infrastructure. In the context of this article, infrastructure means systems. This includes equipment and operational databases and information networks. Many safety and environmental regulations (e.g., process safety management, risk management plans and hazard communications) have implicit data requirements, such as emissions inventory, operating rates, safety data sheets and equipment

data. With the addition of CO₂ capture projects, the need for infrastructure will become more acute. To maintain optimal operations, relevant and reliable information should be quickly accessible. A corollary to this requirement is that database systems and information technology (IT) infrastructure should be user friendly. Inefficiencies and inadequacies of these systems impact productivity and could also impair safety.

Geopolitical considerations. Although geopolitical stability may be hard to quantify and is typically not part of a safety/environmental professional's involvement, large-scale CO₂ capture projects in locations that could be impacted by geopolitics should be carefully reviewed.

Takeaway. Company executives and safety/risk managers recognize that climate change issues and policies could become mired in intense debates, false narratives, regulatory bureaucracy, socioeconomic disruptions and business uncertainty. However, they also see the

need for a rapid but risk-managed transition to low-carbon or zero-carbon technologies. The need for such a transition merits careful consideration. This type of rapid transition could be enabled by a strong infrastructure for project management, data analytics, risk minimization, digitization and a trained and cohesive workforce. Organizations should consider multiple risk assessments at various stages of the project or important milestones. As the project progresses, risk assessments (e.g., hazard and operability analysis, layer of protection analysis and safety integrated level assessment) will address tactical safety, environmental and operational issues. Therefore, the long-term success of CO₂ capture projects requires focused attention on strategic and tactical issues. 

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Up to the 1930s: Whales, lamps, automobiles, plastics and war

Over the next 10 mos, *Hydrocarbon Processing* will provide a detailed history of the origins and evolution of the hydrocarbon processing industry (HPI). This robust analysis will chronicle the beginnings of the modern refining and petrochemical industries through the technological advancements that have created the global energy juggernaut the industry has become today. This examination of the history of the HPI will dictate how human ingenuity has provided the products that have increased the standard of living for billions of people around the world, as well as a reflection on technological advancements over the past 170 yr.

The discovery of kerosene. Everything has a beginning. From the construction of roads, buildings and ship assembly to use in medicines and weaponry, ancient civilizations have been using oil for thousands of years. However, the modern refining industry traces its origins back nearly 170 yr, with the invention of kerosene by Canadian physician and geologist Abraham Gesner and the construction of new refining facilities to produce the high-demand product.

In the early 1840s, Gessner began experimenting with hydrocarbons, specifically bitumen from Trinidad. From these experiments, he developed a process to extract oil, which could be burned.¹ However, the bitumen product was expensive to obtain and the burning of it produced a horrendous odor. Therefore, he started experimenting with a type of asphalt called albertite. Gessner noticed that the oil that was extracted—the process was done by heating coal in a retort²—burned with a strong yellow flame with no odor. He termed the product “keroselaion” from the Greek words “wax oil.” He later shortened the name to

kerosene. Little did Gesner know that his discovery was soon to usurp whale oil in the burning of lamps and begin an international movement.

Whales, lamps and refineries. Through the late 1800s/early 1900s, whale oil was used extensively as a fuel for lighting. The oil, which is more of a liquid wax, was obtained from the blubber from the head of whales. The oil was processed and sold as a fuel for lamps, lubrication, making soap or to produce candles. Although highly dangerous, the whaling industry grew significantly as consumer demand for oil to fuel lighting expanded exponentially.

The whaling industry peaked in the 1820s and declined over the next several decades. Decreasing whale populations and taxation led to higher prices for whale oil, which could not compete against other options, such as kerosene. Consumers’ pocketbooks dictated the pathway to the adoption of a cheaper and comparable alternative, ushering in a new era of refined products.

Several years after Gesner’s discovery of kerosene, Samuel Kier began his own experimentation on petroleum that would seep into his family’s salt wells near Pittsburgh, Pennsylvania (U.S.)—at the time, this substance was known as “carbon oil.” Although the substance could be burned for lighting, much like Gesner’s experiments with bitumen from Trinidad, the unrefined material had an unpleasant odor. Instead, Kier used the material for medicinal purposes until it lost its appeal in the early 1850s.

To find another path for the oily substance, Kier experimented with using the substance for lighting. On the recommendation of James Booth, a chemist and professor from Philadelphia, Penn-

sylvania (U.S.), Kier used distillation to extract the best materials for the use of lamp burning fuel. In 1851, Kier began selling his lamp fuel oil for \$1.50/gal, a more cost-effective product than whale oil.³ As demand grew, Kier established North America’s first oil refinery in 1853, which processed 1 bpd–2 bpd of liquid petroleum in its first year, growing to 5 bpd in 1854 (FIG. 1). In 1859, Edwin Drake drilled the first commercial oil well in North America in Titusville, Pennsylvania. After trial-and-error, he discovered oil at a depth of nearly 70 ft. Soon, his commercial well produced 25 bpd. The oil was destined to be sold to a local refiner to produce kerosene for lamp fuel. His first customer: Samuel Kier.

Nearly 4,300 mi away, Ignacy Łukasiewicz started to produce kerosene in the early- to mid-1850s, as well. After experimenting with different oils extracted by wells drilled near Bóbrka, Poland and other sites he set up with local business entities, Łukasiewicz opened Europe’s first oil distillery in 1856 in Jaslo. The refinery was established to produce kerosene for lamp lighting. Shortly thereafter, a larger scale refinery was built in Ploiești, Poland by brothers Teodor and Marin Mehedințeanu.⁴ The Râfov refinery used cylindrical iron and cast iron vessels, which were heated by wood fire, to produce 7 tpd of distilled oil.⁵ The oil was ultimately used as lamp lighting fuel, leading Ploiești to become the first city to be lighted by distilled crude oil.⁵

In the 1860s, John D. Rockefeller established and increased the size, wealth and power of Standard Oil Company, which produced and shipped kerosene, eventually becoming a monopoly within the U.S.—the company was eventually split into several entities that would lead to the creation of Amoco, Chevron,

Exxon, Mobil and Marathon. By the mid-1890s, Standard Oil Co. had also become the dominant kerosene exporter to other parts of the globe, such as Asia. However, Standard Oil Co. soon found a competitor in the kerosene trade, a European trading company called Shell Transport and Trading Co.—the company established its first refinery in Balikpapan, Indonesia in 1897 (known as Dutch Borneo at the time).⁶ In 1901, Shell Transport and Trading Co. merged with a smaller competitor—Royal Dutch—that had set up a sales organization in Asia. The company took the name the

Royal Dutch Shell Group. The company's operations—drilling, exploration and refining—expanded rapidly to various parts of the globe.⁶

As oil exploration began to increase globally, new refineries were being built in various locations worldwide to produce kerosene and gasoline. For example, after oil was discovered by accident in northeast India, the Assam Oil Co. opened the Digboi refinery in Digboi, Assam, India. The refinery, which produced kerosene, was the first refinery in Asia.⁷

In 1908, George Reynolds, backed by English investor William D'Arcy, dis-

covered oil in Persia (modern-day Iran). Four years later, the Anglo-Persian Oil Co. (AIOC) opened the Middle East's first refinery in Abadan, which would become the largest refinery in the world. However, AIOC found it difficult to find a market for its oil, primarily due to intense competition from more established companies (e.g., Standard Oil Co.). The company soon found an ally in Britain's newest Lord of the Admiralty, Winston Churchill. Churchill was assigned to modernize Britain's navy, which included switching from coal-powered ships to using oil. Not wanting to rely solely on Standard Oil or Royal Dutch Shell, Britain signed a lucrative oil deal with AIOC, which resulted in Britain becoming the majority shareholder in the company. A little over 40 yr later, the company adopted the name British Petroleum (bp).⁸

The genesis of synthetic plastics. In the mid-1850s, English inventor Alexander Parkes was conducting research on cellulose—an organic material component in the cell walls of green plants and the most abundant biopolymer in the world at the time. His research/tests, which included treating cellulose with nitric acid and a solvent, led to the creation of Parkesine, the world's first thermoplastic.

A few years later in 1861, English chemist Thomas Graham discovered a new substance while dissolving organic compounds in solutions. He noticed that some of the substance (e.g., cellulose) would not pass through fine filter paper, leaving behind a sticky residue. He termed this substance "colloids" after the Greek word for glue. The use of colloids led to research that would lead to the birth of new plastics technologies and commercial production.

The American inventor John Wesley Hyatt acquired Parke's patents and began experimenting with colloids and natural polymers. In 1870, he discovered celluloid—one of the world's first plastics—by applying heat and pressure to a mix of cellulose nitrate and camphor. In the late 1880s, French engineer and industrialist Count Hilaire de Chardonnet used a nitrocellulose solution to create "Chardonnet silk," which was a synthetic silk and the basis for rayon—rayon fibers are still produced and less flammable than the ones produced in the 1890s.⁹

Up until the early 1900s, plastics were produced using organic materials.



FIG. 1. Samuel Kier standing next to his 5-bpd petroleum still. Photo courtesy of the Drake Well Museum.

That changed in 1907 with the discovery of Bakelite by Belgian chemist Leo Baekeland. His process involved reacting phenol and formaldehyde—in the presence of a catalyst—under pressure at high temperatures, which occurred in his innovative Bakelizer—a steam pressure vessel (FIG. 2). The result was an extremely versatile resin that could be molded and shaped. This invention was the world's first synthetic plastic.¹⁰ Five years later, Swiss chemist Jacques Brandenberger invented Cellophane—a transparent sheet made from cellulose, which was primarily used as a packaging material. Around the same timeframe, German chemist Friedrich Klatte patented a method for polymerization of vinyl chloride to produce polyvinyl chloride (PVC). **Note:** PVC was first discovered in the 1870s by the German chemist Eugen Baumann but never patented.¹¹

A new process for fertilizer production. Using fertilizers for agricultural significantly expanded in the 1800s/early 1900s. However, the primary sources to develop ammonia—niter and guano—were not adequate to satisfy demand; therefore, a new process was needed to produce adequate amounts of ammonia and nitrates. This challenge was solved by the German chemist Fritz Haber in 1909 and later commercialized and expanded by Carl Bosch of BASF. Baden Aniline and Soda Factory (BASF) traces its roots back to 1865. The company started as a producer of dyes and inorganic chemicals, and, at the turn of the century, added ammonia production to its products portfolio.

The first industrial-scale production plant based on the Haber-Bosch process began operations at BASF's Oppau facility in Germany in 1913 (FIG. 3). This process—still in use today—enabled BASF to become the first company to employ high-pressure technology.¹² The process was also employed in the production of nitrates for munitions during World War I (WWI). The Oppau facility's success with ammonia production expanded to include a second site in Leuna, Germany. This site would not only utilize the Haber-Bosch process to produce ammonia but would also be instrumental in the research and development of synthetic gasoline from the hydrogenation of lignite (i.e., the Bergius process, the fore-

runner to the Fischer-Tropsch process). Other ammonia process pioneers (e.g., the Italian chemist Luigi Casale) would create their own technologies in later years, which would compete against the Haber-Bosch process.

The internal combustion engine (ICE). The production of kerosene included byproducts, such as straight-run naphtha, the forerunner to gasoline.¹³ At the time, this product was usually discarded since there was no clear intended use for the material. However, the onset of the ICE changed the nature of oil refining, as it created an outlet for a byproduct that, at the time, had no real use.

Early pioneers of ICE designs include the French-born Swiss inventor François Issac de Rivaz, French brothers Claude and Nicéphore Niépce and English inventor Samuel Brown. De Rivaz's design— invented in 1807—used an electric spark to ignite hydrogen and oxygen.¹⁴ Although his design led to the first ICE incorporated onto a carriage (a primitive automobile), it was never commercially successful. In the same year, the Niépce brothers patented their own ICE design. The Pyréolophore used a mixture of lycopodium powder, coal dust and resin for ignition purposes.¹⁵ The brothers proved the concept of their design by conducting a test run of their ICE on a boat on the Saône river in France. The successful test led to the brothers receiving credit as the first to use an ICE on a boat.

Samuel Brown is also one of the earliest developers of the ICE (his engine

used hydrogen as a fuel to propel a carriage up to 7 mph in 1828 and a river boat up to 6 knots in 1827). Belgian engineer Étienne Lenoir's ICE design was a single-cylinder engine that used the ignition of coal gas and air to create power that drove the pistons.¹⁶ Although inefficient, the concept led to the creation of the Lenoir gas engine and the production of rudimentary automobiles—the engine was also used for power generation.



FIG. 2. The Bakelizer, the pressure vessel Leo Baekeland used to produce the world's first synthetic plastic. Photo courtesy of the U.S. National Museum of American History (Smithsonian Institution).

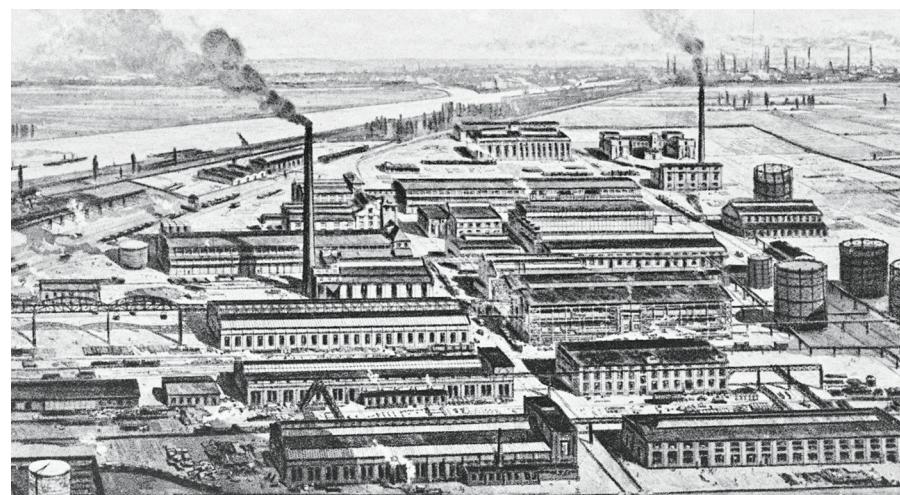


FIG. 3. View of the world's first ammonia synthesis plant. BASF opened the facility in Oppau, Germany in 1913. Photo courtesy of BASF.

Building off Lenoir's design, the German engineer Nicolaus Otto created a four-stroke piston cycle ICE in 1876. Otto's thought process was the inefficiencies in Lenoir's engine design could be solved using a liquid fuel. Gottlieb Daimler and Wilhelm Maybach—both worked at Otto's engine company in Germany in the late 1860s/early 1870s—patented their own ICE design in 1883. Their concept used ligroin (i.e., heavy naphtha) as fuel. Over the next 2 yr, Daimler and Maybach optimized their ICE design by including a carburetor that mixed gasoline with air for combustion.¹⁷ This design led to the

first installation of a liquid petroleum-fueled automobile.

Other engine pioneers improved on earlier ICE designs. For example, Rudolf Diesel designed a more efficient ICE in the early 1890s. His engine could use several types of fuels but primarily used kerosene. The concept significantly improved energy efficiency vs. other engine types, especially those run off steam or gasoline. Diesel's engine was later used in heavier industrial and transportation applications such as agricultural machinery, marine vessels, locomotives, trucks and many others.

Thermal cracking evolves the refining process. As the production of automobiles increased, giving rise to automobile pioneers such as J. Frank, Charles Duryea, Henry Ford, William Durant, Karl Benz and several others, refined gasoline demand surpassed kerosene demand in the early 1900s. This new form of gasoline was refined, unlike previous iterations of straight-run gasoline, which was a byproduct from the kerosene production process. However, the kerosene production process used a simple distillation technique, which did not yield enough gasoline fraction to meet burgeoning demand. This challenge was solved by the invention of the thermal cracking process.

The earliest thermal cracking process was patented by Vladimir Shukhov in Russia in 1891. The Shukhov Cracking Process used high pressure to "crack" heavier hydrocarbon chains into lighter, shorter chains.¹⁸ However, Shukhov's process found little adoption since a market for lighter fraction fuels (e.g., gasoline) did not exist at the time. It was not until the worldwide growth of automobiles did gasoline demand increase in prominence.

In 1910, Americans William Burton and Robert Humphreys developed their own thermal cracking process while working at Standard Oil of Indiana's Whiting refinery—the refinery was originally established to produce kerosene for lamps. According to literature¹⁸, the process involved heating crude oil in a still to 371°C–399°C (700°F–750°F). The petroleum vapors were regulated through a valve system that maintained constant pressure through the entire process. Once the fractions were evaporated, they gathered through a condenser. Lastly, the still was opened and the carbon deposits were collected. The process produced primarily gasoline, gasoil, residual fuel oil and petroleum coke.¹⁸ A view of Burton's apparatus for the process, submitted to the U.S. Patent Office in January 1913, is shown in FIG. 4. The process significantly expanded the Whiting refinery and led to many other refining companies licensing the thermal cracking technology from Standard Oil of Whiting. The Burton process was used extensively for more than 20 yr, until the creation of catalytic cracking. It was not until after WWI that advances to the thermal cracking process accelerated within the industry. **Note:** One of the earliest pioneers in catalytic cracking was the American Almer M.

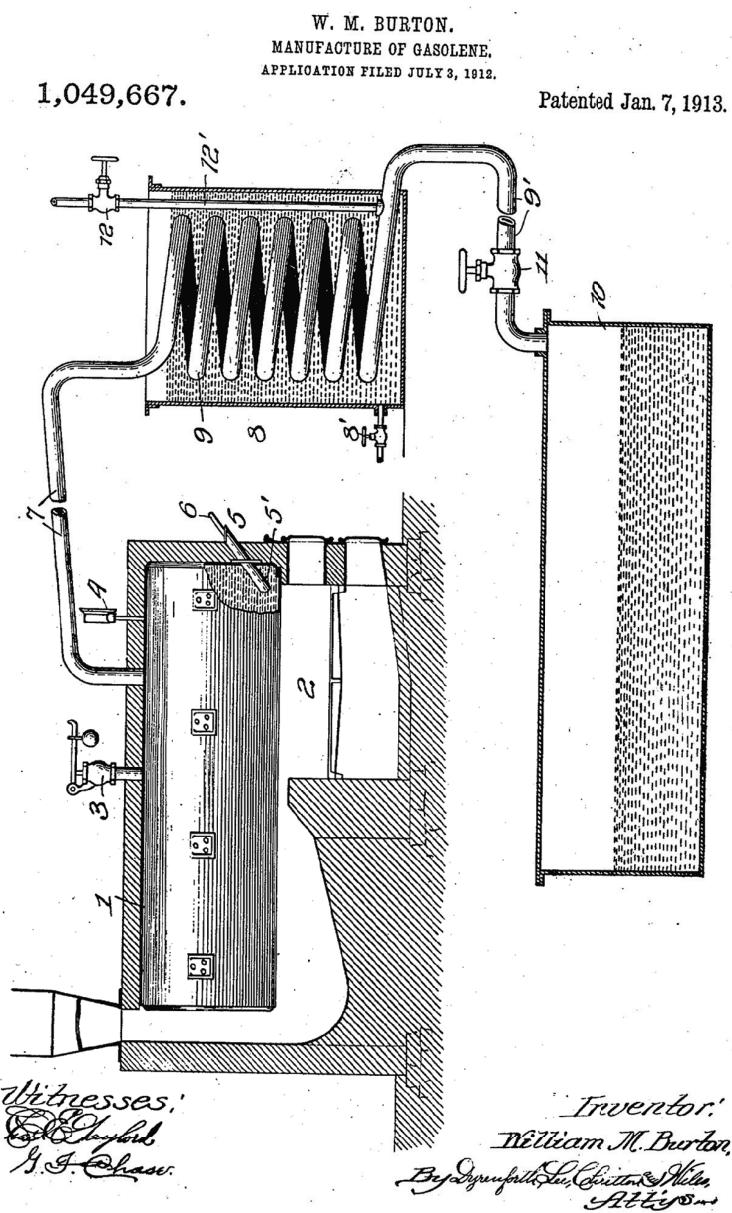


FIG. 4. View of Burton's patented apparatus for gasoline production. Photo courtesy of the U.S. Patent Office.

McAfee, who created a process that used anhydrous aluminum chloride-based catalyst that produced a higher yield of gasoline from the distillation process. McAfee's employer, Gulf Refining, would launch the first anhydrous aluminum chloride cracking unit in Port Arthur, Texas in 1915.¹⁹

In the same year Burton was patenting his thermal cracking process, German scientist Friedrich Bergius developed a new synthetic fuel process. The direct coal liquefaction process—a predecessor to the Fischer-Tropsch process, which used an indirect method for coal liquefaction—involved reacting hydrogen at high pressures with lignite to produce liquid fuels.²⁰

National defense: War ushers in a new era for oil. Prior to the start of WWI, coal was the dominant source of fuel for marine vessels, especially for navies. However, the benefits of using oil soon became prevalent around the world. The fuel had double the energy intensity of coal, refueling at sea was easier, it enabled better flexibility in changing speeds, fewer crew members were needed to operate a ship's fueling system and oil produced less smoke than coal—an imperative for line of sight when aiming cannons at enemy vessels.²¹

In 1914, WWI began in Europe. The 4-yr conflict significantly expanded the use and demand for oil. The war effort included the use of tens of thousands of trucks, motorcars and motorcycles, hundreds of ships and the introduction of airplanes and tanks, all using ICEs that ran off gasoline and used oil for lubrication. The use of oil became a mainstay for transportation, which continued after the war.

Demand increases and technologies advance. As WWI ended, global gasoline demand expanded immensely. Although thermally-cracked gasoline was the dominant choice in ICEs, premature combustion caused knocking, which can cause several problems with an engine's operation. New research efforts were devoted to find solutions to this challenge. This included optimizing the thermal cracking process. C. P. Dubbs created a modified thermal cracking process (i.e., the Dubbs process) that operated at 400°C–460°C (750°F–860°F), which lessened carbon buildup in the system, enabling the process to operate longer before cleanout. Dubbs licensed his process for nearly two

decades under the company name National Hydrocarbon Co., later changing the name to Universal Oil Products (UOP).²²

In 1921, while working at General Motors, Thomas Midgley—who later also helped invent Freon—discovered that incorporating tetraethyllead (TEL) into gasoline prevented knocking in ICEs (increasing gasoline octane rating leads to better compression and, in turn, improved engine performance). Around the same timeframe, chemists at Standard Oil Co. of New Jersey produced isopropyl alcohol (IPA), which is credited as the first commercial petrochemical—it was a synthetic alcohol. Just one year later (September 1922), the inaugural issue of *The Refiner and Natural Gasoline Manufacturer* was published to provide technical articles and know-how to the global refining industry (later including petrochemicals and gas processing/LNG technical materials, as those industries evolved). The publication would change its name several times—evolving with discoveries in new industrial processes—before taking the name *Hydrocarbon Processing*.

Several other technological advances in refining and petrochemicals production happened in the 1920s. These included the discovery of synthetic rubber (styrene-butadiene rubber or SBR) by the German chemist Walter Bock, synthetic methanol by the German chemist Matthias Pier, the production of moisture-proof cellophane, the Fischer-Tropsch process for liquids production (coal liquefaction and gas-to-liquids), the discovery of silicones, an improved method to produce PVC by the American inventor Waldo Semon, the first ethylene plant built by Union Carbide in West Virginia (U.S.), and early research by French inventor Eugene Houdry that would eventually lead to the development of the catalytic cracking process in the 1930s.²³ These milestones in the refining and petrochemicals industries helped provide the foundation for the acceleration of the industry to develop new and better products for the global population.

The 1930s. Over the following decade, the global HPI continued to evolve and advance technologies for fuels and petrochemicals production. The industry's milestones of the 1930s will be discussed in the February issue of *Hydrocarbon Processing*. HP

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100+ years of industry safety

Established in 1919, the American Petroleum Institute (API) represents all segments of the natural gas and oil industry with its nearly 600 members that produce, process and distribute the majority of America's energy. API was established as a standards-setting organization to drive safety and continuous improvements in industry operations. The Global Industry Services (GIS) division of API sets those standards and administers training, certifications and safety programs around the world.

API'S ORIGINS

API's origins can be traced back to World War I when Congress and the natural gas and oil industry worked together to help the war effort. The industry's supply of fuel highlighted its importance to the country and obligation to the public, and the American Petroleum Institute was established as a result.

At the outset and still true today, API was built to encourage cooperation with the government in all matters of national concern, foster foreign and domestic trade of American petroleum products, promote the interests of the petroleum industry and improve the sciences and practices connected with the industry.

WORKING FOR COUNTRY AND INDUSTRY

In 1969, API made its home in Washington, D.C., to better represent the natural gas and oil industry that today supports more than 11 million U.S. jobs and nearly 8% of the U.S. economy. API's nearly 600 members include large integrated companies, exploration and production, refining, marketing, pipeline and marine businesses, as well as service and supply firms. The U.S. energy industry, including API members, has consistently been at the forefront of powering positive change. The recent energy revolution has not only made the United States the world's leading producer, refiner and exporter of natural gas, but it has also put our industry at the forefront of efforts to lower emissions while spurring economic growth and job creation.

SETTING THE STANDARD

To power this change, API has published more than 700 standards to help drive operational safety, environmental protection and sustainability. These standards enable indus-



try to manufacture superior products, provide critical services, help ensure fairness in the marketplace and promote the acceptance of best practices by industry and governments around the world.

The first API standards, published in 1924, was developed to mitigate delays experienced during World War I by creating uniformity in pipe sizes, threading and coupling. Since then, API has published standards that support all aspects of the industry – from manufacturing and supply to pipelines to refining and delivery of product to end-users.

IMPROVING EFFICACY ONE PROGRAM AT A TIME

API's standards lay the groundwork for training, individual and product certifications, and other safety programs. To help ensure industry personnel are knowledgeable in their field, API offers training courses as well as Individual Certification Programs (ICP) that test and certify inspectors in various industry areas including pipelines, pressure vessels and more. Programs like API Monogram, APIQR and Engine Oil Licensing and Certification System (EOLCS) help ensure that the manufacturing of products and the products themselves meet the requirements to keep operations safe, reliable and sustainable.

Additionally, as part of the industry's ongoing commitment to continuous safety

improvements, API's Process Safety Site Assessment Program (PSSAP®) and Pipeline Safety Management System (SMS) Assessment evaluate a facility's process safety systems or pipeline SMS respectively, and create industry benchmarking to share best practices help improve overall safety performance.

NEXT STEPS TOWARD OPERATIONAL EXCELLENCE

These API standards and the programs built around them provide a framework for industry operations, and now, API Energy Excellence® codifies these to take a management system approach to further accelerate safety and environmental progress.

API members commit to 13 core elements, from Leadership Commitment to Operational Integrity, Management of Change and Emergency Preparedness and Response, by applying standards, implementing workforce training and participating in performance initiative. API Energy Excellence is API members' commitment to enhancing the integrity of operations across the industry, while meeting global demand for adorable, reliable and cleaner energy.



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CENTRIFUGAL COMPRESSORS

Elliott compressors are core components of energy-related plants around the world, delivering state-of-the-art performance in a diverse range of industries. Elliott's portfolio includes a number of engineering firsts, including refrigeration compression, high-pressure casing technology, development of fabricated casings, and improved impeller welding techniques.

Optimizing performance is vital to sustainable development and Elliott Group is committed to that effort. Today, Elliott compressors incorporate advances in aerodynamics, rotor dynamics, thermodynamics, and metallurgy that improve efficiency and help to reduce emissions. Recent compression innovations include carbon capture and sequestration, hydrogen processing, and hydrogen energy storage applications, and a proprietary compressor performance prediction tool.

STEAM TURBINES

Elliott steam turbines provide exceptional value and performance in a broad range of mechanical and power generation applications. With a reputation as the most rugged, reliable and versatile drivers in the industry, they are built to perform and endure years of continuous service. These units can be built to API standards and customized to meet exacting customer specification.

Generators powered by Elliott steam turbines deliver reliable, efficient, and cost-effective on-site power to a wide variety of industrial, commercial and institutional users, both on and off the grid. Combined heat and power, co-generation, waste-to-energy, waste heat recovery, and geothermal applications provide alternative sources for clean, renewable power.

Elliott power recover expanders efficiently capture waste flue gas from the fluid catalytic cracking (FCC) process and convert it to energy to reduce a facility's carbon footprint.

CRYOGENIC PUMPS & LIQUID EXPANDERS

Natural gas is an essential and abundant building block of a low carbon, clean energy future. Elliott's cryogenic pumps and expanders help to safely and efficiently meet growing demands for LNG through liquefaction, transport, storage, and regasification applications that maximize production and reduce emissions. For over 40 years, Elliott's Cryodynamic Products business has delivered continuous advances in equipment design and technology to customers around the world. Cryodynamic Products developed the first submerged cryogenic expander in 1997, the first two-phase expander in 2001, the first two-phase tandem installation in 2008, and the first floating application in 2011.



Elliott Centrifugal Compressor in Propane Dehydrogenation Service at a China Petrochemical Plant

In October 2021, Elliott held a ribbon cutting to commemorate the start of commercial operations at its new, state-of-the-art cryogenic pump testing facility. There is no other cryogenic testing facility like it anywhere in the world. As liquefaction plants continue to grow larger in size to meet demand, the new test facility provides the capability to test a full range of cryogenic pumps and liquid expanders, including units larger than those currently available in the industry. With thousands of installations worldwide, Cryodynamics® is the recognized global leader for submerged electric pumps and expanders in liquefied gas and aggressive fluid applications.

GLOBAL SERVICE

In addition to its full line of rotating equipment, Elliott offers complete service packages including parts, repairs, emergency response, scheduled outages, service engineering, modifications & upgrades, training, and customized research. Regionally based field service teams provide local service with the expertise and support of a world-renowned global service organization.



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Saint-Gobain NorPro: A Long Legacy of Supporting the Hydrocarbon Processing Industry

Saint-Gobain NorPro has been servicing the petrochemical, chemical, refining, environmental and gas processing industries for more than 150 years. The business was founded in 1859 by Frank J. Knapp who started a small pottery at his home in Akron, Ohio. The business was named The United States Stoneware Company. As the nation expanded, so did U.S. Stoneware. A group of Akron industrialists, including Jonathan Brewster, George Laudenslager and J.M. Wills, began to provide additional capital needed to meet the increasing volume of orders. In 1885 the firm was incorporated. At that time, some 30 potters were turning out the extensive line of butter crocks, vinegar jars, bed chambers and churns, which were the mainstay of the company's business.

EXPANSION AND GROWTH IN THE AMERICAN CHEMICAL INDUSTRY

The U.S. Stoneware Company was nearly felled by the short depression which began in 1907 as common stoneware sales dropped to an all-time low. Wills, then acting superintendent, sensed he was in a declining business, and explored new markets for clay products. The American chemical industry, then in its infancy, showed great growth potential, and stoneware showed excellent resistance to chemical attack. Wills, and his son-in-law, John J. Chamberlain, pioneered the development of chemical stoneware.

The American chemical industry was forced to expand quickly during World War I, and U.S. Stoneware began producing the large volume of chemical resistant crocks and a number of other products needed to support the war. The plant located then on Annadale Avenue was enlarged, and the Ohio Stoneware company was absorbed. Later the Sperry Pottery plant on West Avenue in Tallmadge, Ohio was purchased and became U.S. Stoneware's headquarters. Additional acquisitions in the 30's included an old pottery in Ravenna, Ohio and Conneaut Rubber and Plastics. U.S. Stoneware also purchased Federal Refractories Corp. in Mineral City, Ohio in 1940. As an extension of work in ceramics, U.S. Stoneware began to design and manufacture mechanical equipment such as mill jars and bar mills. Bathroom fixtures and accessories, porcelain raschig rings, cyclohelix spiral rings for packed towers and ceramic balls used for catalyst support beds were also produced at U.S. Stoneware's various facilities. The development of the ceramic *Intalox® saddle in the 50's introduced a new design which increased tower efficiency and capacity by as much as 50%. This revolutionary packing paved the way to U.S. Stoneware's (and later Norton's) position as an industry leader in random dumped tower technology.

Expansion continued in the 50s including adding a metal fabricating plant across the street from the company headquarters. This facility produced metal trays and tower internals used in the chemical processing industry. R.C. Stamping in Canal Fulton, Ohio was acquired in 1959, enabling U.S. Stoneware to begin production of metal tower packings, strengthening its presence in the chemical industry.

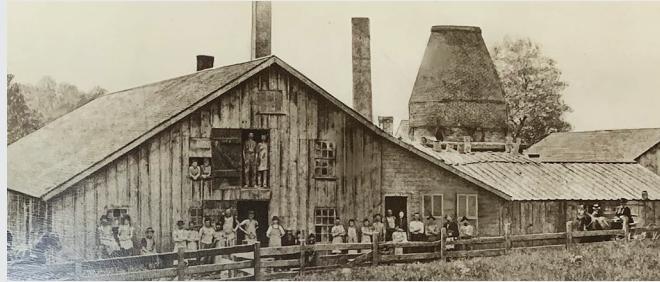


FIG. 1. The United States Stoneware Company located in Akron, OH 1800s

NORTON COMPANY ACQUISITION—1966

By 1965, U.S. Stoneware had 15 plants in Ohio and Tennessee as well as a state-of-the-art research and development center in Stow, Ohio. These plants produced a diverse range of products including their mainstay: ceramics and plastics. Jim Chamberlain's failing health laid the foundation for the sale of the company, and in August 1966, The U.S. Stoneware Co., and its affiliated company, Chamberlain Engineering Corp., were acquired by Norton Company of Worcester, Massachusetts. The company then became known as Norton Chemical Process Products (Norton CPPC). The business grew more broadly to include not only ceramic random packing for heat and mass transfer applications, but also custom catalyst carriers and catalyst bed support media for refining, gas processing and petrochemical applications. A number of market-leading products including the well-known Denstone® 57 support media product was developed during these years.

SAINT-GOBAIN ACQUISITION—1990 TO PRESENT

In 1990, Norton CPPC was acquired by Saint-Gobain, one of the largest industrial corporations in the world. At that time the Norton CPPC name was changed to Saint-Gobain NorPro, to reflect the change in ownership and direction.

A number of support media products were developed in the 1990s and 2000s including Denstone® 2000, Denstone® 99 and Denstone® deltaP® along with MacroTrap® bed topping media. Saint-Gobain has also developed many technical advancements in catalyst carriers including the company's newest innovation, Accu® spheres catalyst carriers, which were commercialized in 2017. Today Saint-Gobain NorPro remains a global leader in supplying engineered ceramic media and shapes to the chemical industry, operating seven world class manufacturing facilities on three continents along with a state-of-the-art research and development center and their global headquarters located in Stow, Ohio.

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Advancing processing technologies and refining operations: Excerpts from the 1920s

The following is a mixture of technical articles, columns and headlines published in the 1920s by *The Refiner and Natural Gasoline Manufacturer*, the forerunner to *Hydrocarbon Processing*. This collection of excerpts provides a look into the major technological advancements and topics/trends in the hydrocarbon processing industry during that timeframe.

Comparison of principles involved in existing cracking processes

L. Reiss and E. R. Lederer, January 1923

This article detailed the nine different classifications under which cracking processes fall:

1. Cracking in stills under pressure
2. Cracking in the liquid phase in tubes under pressure
3. Cracking in the liquid-vapor phase in tubes under pressure
4. Cracking by any of the above, using steam
5. Cracking by any of the above, using fixed gases and hydrogen
6. Cracking by any of the above, using chemicals
7. Cracking with the aid of internal heat
8. Cracking in the vapor phases in tubes under pressure
9. Cracking by electrical methods.

Some advantages of Dubbs Cracking Process

E. R. Lederer and W. F. Fulton, February 1923

The authors detailed the advantages of the Dubbs Cracking Process. Most notably, the Dubbs plant has the advantage of being able to handle up to 20 t of carbon or coke, which is deposited out of the heating zone in the expansion chamber where it can be easily removed at the end of the run without any material injury to the apparatus, thus permitting continuous operation over a longer period than any of the other methods in commercial use at the present time.

High recovery claim of Cross process

R. Cross, March 1923

During the early 1920s, many companies were conducting research to increase gasoline yield in refining. The author wrote, "Never in the history of the petroleum industry has there been so much activity in methods of increasing the yield of gasoline from crude oil. During the last 12 mos, most important advances in practical cracking have been made." This article provided details on a new process, which essentially is a process of producing synthetic crude that is subsequently distilled.

Blending distillates and gas condensates

G. W. Reid, April 1923

This article provided new insights on the blending of petroleum distillates and natural gas condensates. The primary purposes of the author's experiments were to detail physical changes that occurred when blending is in process and distillates and condensates are being mixed. Are the changes purely physical, purely chemical or a mixture of both?

Copper dish and "doctor" tests not so good

J. V. Meigs and E. J. Ford, May 1923

The authors provided insights on how the present way of determining corrosive elements in gasoline could be greatly improved, as well as offering their opinion on better methods.

Editorial Comment: Can there be too many cracking plants?

R. L. Dudley, June 1923

What will be the result if most refineries install cracking plants? Won't this mean an over-production of gasoline with resultant lower prices? These questions were answered within a survey conducted by the publication in 1923. The majority response was, "yes, more cracking processes probably will lower the cost of gasoline if the present supply of crude continues, but economically and financially the cracking process will be vindicated more as the years go by."

Cooling condensing water a problem

H. Pennington, April 1924

The value of cool condensing water is felt by every refiner running light oils, especially during summer months when atmospheric temperatures run high, and condensers are apt to "blow." This challenge is not always given much attention but has a prominent place in operating efficiency.

Comparing gasoline plant operating costs

D. E. Foster, April 1924

The big problem of a gasoline plant is not simply running the plant and making gasoline, it is making money on the invested capital. This article detailed the economics of three methods of producing natural gasoline in 1924: compression, compression-blending and oil absorption.

Power costs reduced by electric drive

H. Pennington, August 1924

This discussion covered the application of steam turbine-driven generators for refinery operations in such a way that the steam is given superheat in the boilers, put through the turbine, where power is skimmed from it, and the steam is reduced in pressure, then passed out into the header, supplying stills with naked steam for distillation purposes.

Refining without shutdown for rerun

G. W. Reid, September 1924

From a study of approximately 40 refining plants, it is evident that progress is being made toward the accomplishment of taking care of rerun distillates without shutting down the plant during crude oil runs. Circulating distillates through towers prevents the accumulation of stocks and increases recovery.

Gasoline being extracted from shale

October 1924

M. J. Trumble has perfected a process for extracting oil and gasoline from shale in an experimental plant located at Alhambra, California (U.S.). The process is cyclic in character; that is, instead of producing the oil from shale in one operation and then distilling the crude oil into gasoline and other products in a second operation, the gasoline is produced from the oil shale through one continuous operation in which the crude oil occupies only an intermediate stage.

Boiler efficiency essential to refining

H. Pennington, November 1924

Temperature regulation for towers

W. C. Begeebing, November 1924

It has only been in the last few years that efficient fractionating towers and reflex condensers have come into general use. Tower construction has been greatly improved and with it has come the widespread adoption of automatic temperature control.

Many methods used in treating operation

C. K. Francis, March 1925

As the demand for higher quality product increases, more knowledge of various systems is being sought. This paper reviewed new methods to increase product purity from the refining process.

Review, comparison of fractionating towers

W. A. Peters, March 1925

This article detailed how the flexibility of a bubble tower can produce the desired product in only one run.

Essentials of plant lubrication

C. A. Fitz-Gerrell, May 1925

The correct type of oil is one that supplies fluidity in the delivery of the maximum of power in an even, steady flow through the stress of all operating conditions. Vital points to consider are maximum load and operating temperatures.

Accounting system for a refinery with a cracking system

R. J. Omo, July 1925

It was found that a cost system was necessary in operating a plant. The system that is described in this article provides the plant superintendent the cost of each step in the manufactur-

ing process, and whether that person was overstepping a pre-determined economic limit, and if so, why.

Fuel oil—Its uses and methods of analysis

August 1925

The use of oil fuel is now becoming general in all trades and industries, the majority of which, were up until a few years ago, entirely dependent on coal. This article detailed the uses of fuel oil—especially in marine travel—and comparing various specifications.

Oil a source of raw material for chemical industries

J. E. Meyer, October 1925

Prevention of evaporation losses from gasoline storage

R. E. Wilson, H. V. Atwell, E. P. Brown and G. W. Chenicek, October 1925

The loss of gasoline from storage tanks with roofs tight enough to keep out the wind is due almost entirely to the daily breathing out of gasoline-saturated air as the temperature increases.

The future of gasoline

E. J. Ford, December 1925

This outlook provided insights on the next decade of gasoline demand (up to the mid-1930s). The author believed gasoline demand would continue to increase due to the rise in automobile demand—a more convenient way of travel vs. railway—and the increase in air travel. “Probably even more likely is the possibility of larger planes or small dirigibles for interurban transportation. No one will deny that the day of long-distance air travel is fast approaching.”

Decreasing refinery evaporation losses of gasoline

L. Schmidt, March 1926

In 1925, gasoline losses through evaporation totaled approximately 6.3%. However, better equipment and process changes have cut that loss in half. The improvement on various vapor-saving equipment and knowledge will further reduce gasoline losses from evaporation.

Contributing factors to corrosion, with special reference to sulfur

C. K. Francis, March 1926

Sulfur can wreak havoc on a refinery’s operation. No matter how the sulfur was formed in feedstock material, methods must be studied and devised to control and get rid of it.

Proper design and operation of heat exchangers

F. L. Kallum, M. E. Semino and A. F. Semino, April 1926

Production of heat is the costliest item in petroleum heating. Once produced, the conservation of heat offers opportunity for perhaps the greatest saving in the operation of a refinery or natural gasoline plant. This is the primary reason for the development of the heat exchanger in refining circles in the last 5 yr.

How to conserve steam in a refinery

H. S. Bell, May 1926

No matter how efficient a refiner’s boiler house may be, they must use the steam intelligently and without waste to reap full op-

erational benefits. This article provides detailed analysis on the wastes that are often encountered in the steam distribution system and offers suggestions for conserving steam in the refinery.

Cracking heavy hydrocarbons in the presence of catalyst I. Ginsberg, November 1926

Our article is concerned with a discussion of certain results that were obtained in the cracking of heavy hydrocarbons, mineral oils, mineral oil residues, ozocerite and the like into lower boiling products by heating them to the boiling point in the presence of activated charcoal and other catalysts.

Corrosion—An economical refinery problem

H. F. Perkins, January 1927

Only within the last few years have we been informed of the real mechanism of corrosion, and we are now ready to study each case of corrosion individually based on this information and depart from empirical methods.

Centrifugal vs. reciprocating pumps for refinery service

W. R. Layne, March 1927

This work provides a detailed comparison of two pump types: centrifugal and reciprocating. The best economy will be considered that results in the lowest total cost of pumping per barrel.

Refining capacity shifting to integrated companies

G. Reid, June 1927

The use of solvents for dewaxing paraffin-base crude oil

H. M. Smith, October 1927

A method utilizing solvents for the purpose of separating and removing waxy material is described in this article, together with preliminary experiments with solvents that led to its development. The solvents used are secondary butyl alcohol, acetone and mixtures of these, as well as isopropyl alcohol.

Using chemicals protects distillation equipment against corrosion

G. Egloff and J. C. Morrell, December 1927

The economic losses due to corrosion are high. This article considers the injection of chemicals into refinery equipment to neutralize the corrosive substances resulting from the atmospheric and super atmospheric distillation of petroleum oils.

Clays and their application in refining

G. W. Cupit, April 1928

The various benefits of using clays in petroleum refining are discussed in this article.

Automatic control equipment in the modern refinery

C. B. Faught and F. R. Staley, May 1928

A surprisingly large percentage of the total operations in a modern refinery are still classed as manual. However, increasing automatic control on equipment can optimize refinery throughput and efficiency.

Methods of testing gasoline for anti-knock properties July 1928

This table, provided by H. G. Koehler of the Research Labo-

ratories of the Universal Oil Products Co., provide data relative to the various methods of testing gasoline for anti-knock properties.

The plant manager's part in accident prevention

C. W. Price, August 1928

There are three qualifications that are indispensable to a manager who would successfully promote safety at the plant. The plant manager must:

1. Believe in safety as a good business proposition
2. Believe in safety wholeheartedly and express those same principles to the plant workforce
3. Not only initiate a safety campaign but must continuously associate with safety activities.

Natural gasoline outlook brighter: Expansion in cracking facilities indicates large demand and improved market for 1929

H. J. Struth, February 1929

Gasoline plant gathering system design

J. C. Bolinger, April 1929

In the design of pipelines for the transmission of gas, it is necessary to make use of some formula expressing the relations to each other of the quantity, initial and final pressures, diameter and length of line.

Special precautions for handling sulfur crudes at refineries

D. G. Cooper, May 1929

In handling sulfur crudes, hazards to personal safety and severe corrosion of equipment are encountered. Since these hazards exist in nearly all phases of the handling of crudes the utmost care in procedure must be followed.

Is present gasoline storage capacity adequate to best serve the industry?

H. C. Charles, June 1929

Few big companies dominate refinery capacity

G. Reid, July 1929

Nineteen companies control 75% of the total crude capacity and 80% of cracking facilities in the U.S.

The manufacture of commercial anhydrous aluminum chloride

A. M. McAfee, August 1929

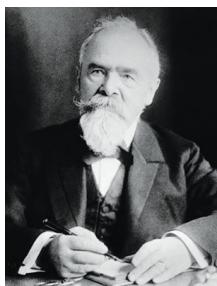
For the first time, in this article, are the details of the aluminum chloride process made public.

Natural gasoline industry expansion slowing down November 1929

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Industry Pioneers: Up to the 1930s

CARL VON LINDE



Carl von Linde was a German scientist and engineer who pioneered new technologies in refrigeration and the invention of air separation and gas liquefaction processes. In the 1870s, Linde's studies led to an efficient design for refrigeration. The first iteration used methyl ether, which was later switched to ammonia. Towards the end of the 1870s, Linde and five partners established the Gesellschaft fur Linde's Eismaschinen (Linde's Ice Machine Co.) in Wiesbaden, Germany. The novel refrigeration device was of extreme importance, especially to the beer brewing industry, as well as the meat industry and cold storage facilities. These inventions quickly replaced ice in many industries, especially in food handling.

In the early 1890s, Linde research shifted to low-temperature refrigeration and the liquefaction of air. This included the technique of obtaining pure oxygen and nitrogen by fractional distillation of liquefied air. In 1895, he successfully liquefied air by compressing it and then letting it expand rapidly, which cooled it. This enabled him to obtain oxygen and nitrogen from the liquified air by slow warming.¹ Several years later, he invented a method for separating pure liquid oxygen from liquid air, which provided oxygen to various industries.² These discoveries led to the creation of Linde Air Products in the U.S. in 1907, which later became part of the Union Carbide company at the beginning of World War I.³

ABRAHAM GESNER



The Canadian geologist and physician, Abraham Gesner, is credited with the invention of kerosene. In the mid-1830s, he worked as a provincial geologist in New Brunswick, Canada, examining coal in the province. In the 1840s, he began experimenting with hydrocarbons, especially bitumen from Trinidad. From these experiments, he developed a process to extract oil, which could be burned. However, the bitumen product was expensive to obtain and the burning of it produced a horrendous odor. Therefore, he started experimenting with a type of asphalt called albertite. Gessner noticed that the oil that was ex-

tracted—the process was done by heating coal in a retort⁴—burned with a strong yellow flame with no odor.

In 1854, Gesner obtained three U.S. patents for his kerosene fuel and set up the North American Kerosene Gas Light Co. on Long Island, New York (U.S.). The company prospered and kerosene began to be the go-to fuel for lamp lighting, replacing whale oil.

SAMUEL KIER



Samuel Kier was an American inventor and is thought of as the founder of the American refining industry. Several years after Gesner's discovery of kerosene, Samuel Kier began his own experimentation on petroleum that would seep into his family's salt wells near Pittsburgh, Pennsylvania (U.S.)—at the time, this substance was known as "carbon oil." Although the substance could be burned for lighting, much like Gesner's experiments with bitumen from Trinidad, the unrefined material had an unpleasant odor. Instead, Kier used the material for medicinal purposes until it lost its appeal in the early 1850s.

To find another path for the oily substance, Kier experimented with using the substance for lighting. On the recommendation of James Booth, a chemist and professor from Philadelphia, Pennsylvania (U.S.), Kier used distillation to extract the best materials for the use of lamp burning fuel. In 1851, Kier began selling his lamp fuel oil for \$1.50/gal, a more cost-effective product than whale oil. As demand grew, Kier established North America's first oil refinery in 1853, which processed 1 bpd–2 bpd of liquid petroleum in its first year, growing to 5 bpd in 1854. The effects of Kier's refinery not only led Pittsburgh to become the first U.S. city to be illuminated by petroleum, but also led to the start of the country's refining industry.

MARCUS SAMUEL, SAMUEL SAMUEL



In 1870s, the Samuel brothers inherited their father's import-export business. At the time, their father (Marcus Samuel) built a prosperous business of importing shells from the Far East to

be used in interior design.

Around 1880, the Samuel brothers expanded their father's business to include exporting oil around the world. However, a challenge at the time was oil containers and space on a marine vessel. Oil barrels were prone to leak and took up a lot of space on oceangoing vessels. To overcome this challenge, they commissioned a fleet of steamers to carry the oil in bulk.⁵ Just as the brothers were revolutionizing crude oil trade, they began to include shipping kerosene to demand centers around the world. In 1896, the brothers renamed the company Shell Transport and Trading Co.

By the late 1890s, business was booming, and the company established its first refinery in Balikpapan, Indonesia in 1897 (known as Dutch Borneo at the time). In 1901, Shell Transport and Trading Co. merged with a smaller competitor—Royal Dutch—that had set up a sales organization in Asia. The company took the name the Royal Dutch Shell Group. The company's operations—drilling, exploration and refining—expanded rapidly to various parts of the globe and since it has become one of the largest integrated energy companies in the world.

JOHN D. ROCKEFELLER



The American industrialist was responsible for building the largest refining operation in the U.S., which led to the spin-off of several different entities, each becoming some of the largest integrated oil companies in the world.

The company's origins began in the early 1860s. Rockefeller and other associates owned refineries in Ohio (U.S.), producing kerosene for lamp lighting.

Over the next 20 yr, the company expanded exponentially, controlling nearly 95% of refining operations in the U.S. By the mid-1890s, Standard Oil Co. had also become the dominant kerosene exporter to other parts of the globe, such as Asia. However, the company was eventually labeled a monopoly and was split into several entities that would eventually lead to the creation of Amoco, Chevron, Exxon, Mobil and Marathon.

FRITZ HABER, CARL BOSCH



Using fertilizers for agriculture significantly expanded in the 1800s/early 1900s. However, the primary sources to develop ammonia—niter and guano—were not adequate to satisfy demand; therefore, a new

process was needed to produce adequate amounts of ammonia and nitrates. This challenge was solved by the German chemist Fritz Haber in 1909 and later commercialized and expanded by Carl Bosch of BASF.

Haber conducted significant research in the early 1900s on the synthesis of ammonia from nitrogen and hydrogen.

The process requires high temperatures, high pressure and catalysts. Intense research was led by Carl Bosch. After a few years of trial-and-error, the process was a success, and the first ammonia synthesis plant went into operations in Oppau, Germany in 1913.⁷

The Haber-Bosch process—still in use today—enabled BASF to become the first company to employ high-pressure technology. The Oppau facility's success with ammonia production expanded to include a second site in Leuna, Germany. This site would not only utilize the Haber-Bosch process to produce ammonia but would also be instrumental in the research and development of synthetic gasoline from the hydrogenation of lignite.

WILLIAM BURTON



William Burton was an American chemist who is credited for inventing a viable thermal cracking process. In 1910, he and Robert Humphreys developed their own thermal cracking process while working at Standard Oil of Indiana's Whiting refinery—Vladimir Shukhov (Russia) holds the earliest patent for thermal cracking, which he invented in 1891. However, the Shukhov Cracking Process found little adoption since lighter fractions (e.g., gasoline) did not exist at the time.

According to literature⁸, Burton's thermal cracking process involved heating crude oil in a still to 371°C–399°C (700°F–750°F). The petroleum vapors were regulated through a valve system that maintained constant pressure through the entire process. Once the fractions were evaporated, they gathered through a condenser. Lastly, the still was opened and the carbon deposits were collected. The process produced primarily gasoline, gasoil, residual fuel oil and petroleum coke.⁸ The Burton process was used extensively for more than 20 yr, until the creation of catalytic cracking. **HP**

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Impact of biofeed retrofits, coprocessing on refinery amine units, SWSs and SRUs—Part 1

Diesel with a portion of biologically sourced carbon is being produced at an increasing number of conventional crude oil refineries. This is being done by co-processing biofeedstocks in refinery hydrotreaters and fluidized catalytic crackers (FCCs) or through the installation of a dedicated biofeedstock hydrotreater to produce commercial biodiesel products. Generally, refineries are looking to technologies that allow them to easily incorporate biofeedstocks into their existing infrastructure. This article describes the impacts that this incorporation has on a refinery's existing amine system, sour water stripper (SWS) and sulfur recovery unit (SRU), which are used to remove toxic contaminants from the hydrocarbon products, waste vapors and wastewater in the refinery. It also presents some of the operational and design options available to manage those impacts, as well as a specific case study. This article focuses on the operational changes in, and challenges for, amine, sulfur and sour water units in conventional oil refineries due to biodiesel production. This information will be useful for readers looking to predict the impact on these units or to resolve an operational issue resulting from biofeedstock coprocessing.

Refineries, meet biofeedstocks. Toxic hydrogen sulfide (H_2S) is present in hydrogen recycle streams, hydrocarbon products, effluent gas and water streams. Refineries must use a treatment scheme (FIG. 1) to remove it—a system that is mostly standardized across conventional

refineries in service worldwide. The H_2S , carbon dioxide (CO_2) and ammonia (NH_3) are removed from hydrogen and hydrocarbon streams by water washing and amine solvent scrubbing. The amine and water are then stripped by using steam, and the resulting concentrated stream of H_2S , CO_2 and NH_3 is treated in a modified Claus plant commonly called an SRU. In the SRU, the H_2S is converted to elemental sulfur, and most of the NH_3 is broken down to N_2 and H_2O . CO_2 passes through the unit largely unreacted. The liquid sulfur product is further treated and then sold to the fertilizer and sulfuric acid industries. Many refineries will have an additional amine unit—a tail gas treating unit (TGTU)—to recover more H_2S and sulfur dioxide (SO_2) from the Claus tail gas to reduce SO_2 emissions to the atmosphere. While the general scheme is common to most refineries, there are many variations in configuration, technology, solvent type and equipment within the amine treating and SWS units,

and also within the SRUs and TGTUs. H_2S degassing of the liquid sulfur product is not affected by biodiesel coprocessing and, as such, will not be covered in this article. Similarly, the impacts of biofeed coprocessing on the SRU incinerator are minor and can be disregarded.

With stricter limits on CO_2 emissions associated with conventional fuels, bio-based waste oils (such as vegetable oils and liquid intermediates of biomass conversion) have become an interesting subject as an alternative energy source for energy companies. One advantage of bio-based oils vs. crude oil is their low sulfur content; however, their high oxygen content (TABLE 1) presents several processing challenges.

Vegetable oils are the most common biofeedstock in oil refineries. They consist of triglycerides and fatty acids, which contain oxygen in their molecular structure. The presence of oxygen means that these components are already partially oxidized, so their energy density is lower. Although

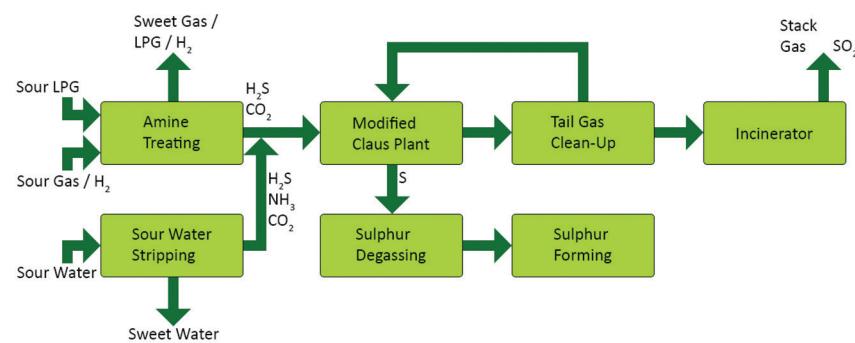


FIG. 1. Conventional refinery treatment scheme.

TABLE 1. Comparison of crude oil to biofeedstocks

Vegetable oil	Pyrolysis bio-oil	Hydrothermal liquefaction	Crude oil
Characteristics			
Triglycerides and free fatty acids	As many as 400 components	Lower oxygen content	
Diesel range lipids	High oxygen	Lower water content	
Metals/inorganics and other contaminants	Variable aromatics levels		
	Water content		
Processing requirements			
Oxygen removal	Oxygen removal	Oxygen removal	
Cracking/isomerization for some products	Cracking of large molecules	Cracking of larger molecules	
Fractionation	De-aromatization	De-aromatization	
	Fractionation		
Compositions			
Carbon, wt%	77.6	54–65	83–86
Oxygen, wt%	10.4	28–40	< 1
Hydrogen, wt%	11.7	5–7	11–14
Sulfur, wt%	0.0006	< 0.05	0.01
Nitrogen, wt%	0.0011	0–0.2	0.095
			–

some bio-based oils can be used directly as a fuel, the process of upgrading for better-quality products is attractive. Upgrading bio-based oil requires the removal or reduction of oxygen atoms. Processing or coprocessing bio-based oils in refineries is a low-cost route because the processing infrastructure, supply chain and distribution network not only support but accelerate bio-based oil production.¹ In refineries, the most likely tie-in points for using bio-based products are the diesel hydrotreater (DHT) and the FCCU.

Alternatively, there are potentially cheaper future feedstocks, such as cellulosic biomass, which can be decomposed using pyrolysis to make bio-based pyrolysis oil. This can be used directly as a fuel for various heaters or further upgraded in the hydrotreater or the FCCU. Pyrolysis oil is dissimilar to its petroleum counterpart, containing approximately 300 different carbon molecules and up to 40% oxygen, which means that it requires significantly more (costly) hydrogen during hydrotreating than lipid-based biofeedstocks like vegetable oil.² Pyrolysis oil is acidic, less stable, contains high amounts of water and has low energy density (H/C ratio = 0.2). A project funded by the European Union (EU)—4Refinery—is investigating the processing of blended vegetable and pyrolysis oil feeds, as these are technically easier to handle in existing

infrastructure than 100% pyrolysis oil. A summary of the different potential feedstock characteristics is provided in TABLE 1.

Coprocessing routes. Industrially, three routes to producing saleable diesel from a mix of biofeedstock and crude (FIG. 2) include:

1. Injecting a drop-in, lipid-based biofeed into the existing DHT
2. Using a purpose-built, standalone vegetable oil hydrotreater, the diesel from which is blended with conventional diesel to obtain the correct product properties (e.g., cloud point)
3. Incorporating a drop-in lipid (and potentially lignocellulosic) biofeed into the existing FCCU.

The first two routes rely on lipid-based biomass, such as vegetable oil, oil crops, algae or tallow—although pyrolysis and hydrothermal liquification oils are both under investigation for future use. Pinho *et al.* carried out test runs on a pilot-scale FCCU for coprocessing vacuum gasoil (VGO)—which is its normal feed—with pinewood chips.³ While lipid feedstocks can be converted relatively easily into biodiesel or green diesel, they are more expensive than lignocellulosic ones. Conversely, they generally contain much less oxygen, meaning less hydrogen demand during hydroprocessing. Furthermore,

the upgrading technology for these compounds is already well-developed in industry and requires a relatively small investment when incorporated into existing refineries. The amount of upgrading required for lipid biomass is related to the desired degree of biodiesel blending.

Direct injection into the DHT. The first process route is the most common. In this route, the lipid biomass is pretreated (e.g., degummed) to remove contaminants before it is added to the DHT. The catalyzed, hydrogen-rich, high-temperature (300°C–400°C) and high-pressure (40 barg–100 barg) environment of the DHT simultaneously deoxygenates the biofeedstock molecules to produce H₂O and desulfurizes the petroleum diesel compounds to form H₂S. CO₂ is also formed through decarboxylation of the biofeed molecules. Methane, propane and carbon monoxide (CO) are also produced as byproducts. The hydrogenated chemical structure produced in this manner has long, unbranched hydrocarbon chains, which results in a biodiesel with a cloud point much greater than petroleum diesel. Therefore, this method of coprocessing will generally only permit a maximum of 10% biofeed before the blended product begins to exhibit cold flow issues.

The Preemraff Göteborg oil refinery in Sweden has successfully coprocessed up

to 30% biofeedstock in its DHT as a summer-only fuel.⁴ However, this was done using a feedstock known as raw tall diesel, which is a processed bioproduct of pulp mills. This product is not equivalent to vegetable oil and is only available in sufficient quantities in some geographical locations.⁵ **Note:** These larger coprocessing proportions required some hydrotreater modifications and solutions to challenges related to hydrogen consumption, exotherm, corrosion and catalyst selection.

Injection into a standalone green diesel unit. The second process route is to produce hydrotreated vegetable oil (HVO) in a purpose-built standalone vegetable oil hydrotreater designed specifically for HVO production. The resulting HVO—known as hydrotreated esters and fatty acids (HEFA)—is then blended with the hydrotreated petroleum diesel. Certain processes that have successfully employed this approach are Honeywell UOP's Green Diesel and Neste Oil's NEXBTL processes. While not technically coprocessing, up to 30% HVO may be blended with conventional transport diesel to produce what is referred to as green diesel. This approach allows for a greater bio-content due to the extra processing in the standalone HVO hydrotreater.

As previously stated, one issue with directly injecting biofeed into the petroleum hydrotreater is the high cloud point of the resulting biodiesel. However, the HVO-specific hydrotreater is a two-stage process. In the first reaction stage, the fats are hydrotreated with hydrogen to saturate the double bonds and deoxygenate the molecules. The second hydrocracking/isomerization stage reduces the length and increases the branching of the alkane molecules. This second stage is also called dewaxing, as this process reduces the cloud point of the resulting HVO so that it is consistent with petroleum fuel specifications and has acceptable cold flow properties. The investment for an HVO standalone hydrotreater is greater than in the first processing approach and uses more hydrogen. However, the HVO product is closer to petroleum diesel and provides greater blending flexibility. The mass yield of HVO liquids from raw lipid material is approximately 80%, with the balance being composed of mostly propane, methane and oxygenated gases like CO₂ and CO. This approach produces

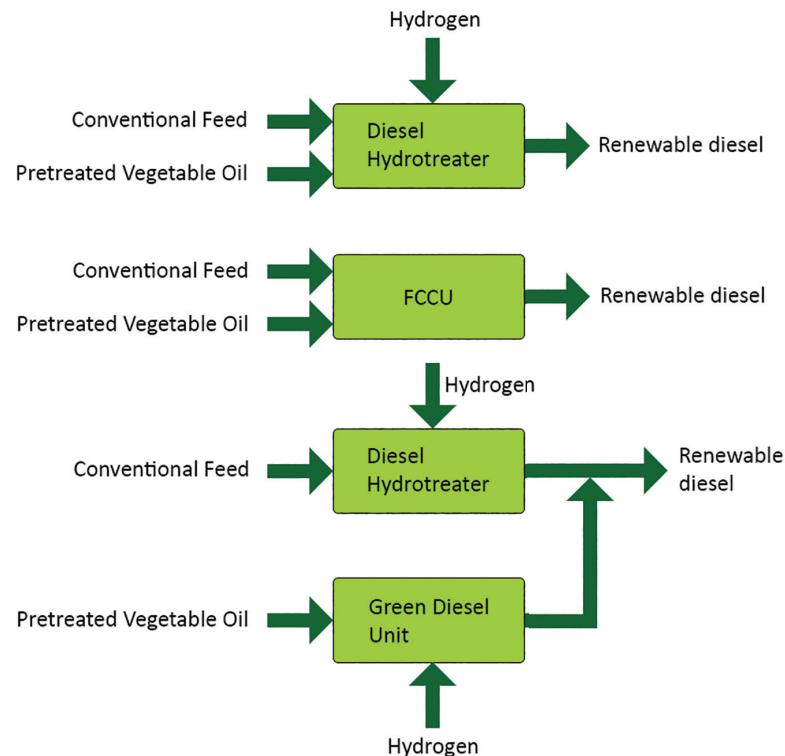


FIG. 2. Three routes for green diesel/biodiesel production.

significantly more propane than the first approach, as the hydrogenation reaction breaks the lipid esters from the propane backbone. A more detailed background is publicly available in the report by Kampman *et al.* for the EU commission.⁶

Injection into the FCCU. The third process route for coprocessing and blending is to co-feed a biofuel with the crude oil to the FCCUs, which operate at approximately 500°C and at low pressures (1 barg–2 barg). The purpose of the FCCU is to crack heavy hydrocarbon molecules into gasoline and some middle and heavy distillate fractions. This point in the refinery is a good candidate for coprocessing because the FCCU does not require expensive hydrogen for deoxygenating the feed. The catalyst is also more tolerant to contaminants than hydrotreating catalyst and can be regenerated on-site. Common problems faced in FCCU processing biofeeds are low yield, catalyst deactivation and reactor plugging.

The vegetable oil cracking mechanism in the FCCU is complex. Unlike in the hydrotreating process, where hydrogen is used to remove oxygenated hydrocarbons to produce water, the FCCU process rejects the oxygen atoms, which results

in the production of H₂O, CO, CO₂ and other oxygenated hydrocarbons³ such as short-chain carboxylic acids, aldehydes, ketones and phenols.⁷ The concentration of these products depends on the bio-based oil type, the FCCU catalyst type, the operating parameters of the FCCU and other factors. TABLE 2 summarizes the impacts of the various processing methods on the quantity and quality of the important liquid and gas streams.

Impacts on amine treating. In conventional refining, hydrogen, fuel gas and LPG streams are contacted with an amine solvent to remove H₂S. The amine solvent will also remove CO₂ and, in some instances, other sulfur species. A simple process schematic of an amine system is shown in FIG. 3. The greatest impact of biodiesel production on amine treating is that the feed gas has more CO₂ and less H₂S.

Depending on the amine solvent used in the refinery, the extra CO₂ generated by processing the biofeed can reduce the quality of the acid gas feeding the SRU, especially at greater co-feed proportions. With primary and secondary amines, the extra CO₂ will normally be removed by the amine solvent to ppm levels in the treated gas or liquid, and there will be a

TABLE 2. Typical process impacts for downstream treating units

Approach	Drop-in hydrotreating	HVO production	Drop-in FCCU
Water volume	Unit size and feedstock dependent. Increases in total facility sour water volume in the range of 10%–25% have been witnessed at 10% coprocessing.	Unit size and feedstock dependent, but large. Increases in total facility sour water volume in the range of 40%–60% have been seen.	Up to 80% of the oxygen present in the feed will convert to H ₂ O. Canola oil: 85% of feed oxygen is converted to H ₂ O. ⁸ Soybean oil: 85% of oxygen is converted to H ₂ O. ⁹ Pyrolysis oil: 78% of inlet oxygen is converted to H ₂ O. ⁹
Water bulk composition	500 ppmw NH ₃ –40,000 ppmw NH ₃ 200 ppmw H ₂ S–20,000 ppmw H ₂ S 200 ppmw CO ₂ –2,000 ppmw CO ₂	500 ppmw NH ₃ –900 ppmw NH ₃ 200 ppmw H ₂ S–400 ppmw H ₂ S 1,200 ppmw CO ₂ –2,000 ppmw CO ₂	Increased CO ₂ and decreased H ₂ S, NH ₃ , HCN and RSH vs. crude oil.
Water trace compound composition	Phosphate and sulfate detected.	Phosphate and other anions expected, but data is not available.	Processing pure vegetable oils in a lab resulted in water with acids ² : Acetic: 900 ppmw–1,700 ppmw Propionic: 600 ppmw–1,400 ppmw Formic: 200 ppmw–300 ppmw Butyric: 10 ppmw–20 ppmw
Gas bulk composition	CO ₂ increased from less than 50 ppmv to 4,000 ppmv to 15,000 ppmv on biofeedstock introduction.	Dedicated hydrotreater has the following ranges: H ₂ S (200 ppmv–6,000 ppmv) and CO ₂ (2 vol%–5 vol%)	Vegetable oil: Higher C ₁ and C ₂ , lower hydrogen yield vs. VGO. ¹⁰ Pyrolysis oil: Hydrogen, methane and ethane decreased vs. VGO. ³
Gas trace compound composition	CO increased from 0 ppm to between 1,200 ppm–4,500 ppm for 5%–10% coprocessing. In some instances, increased coprocessing created more than 1% CO. While not rigorous, a rough relationship of 400 ppmv of CO in the recycle per 1% of biofeed processed appears to hold.		Vegetable oil: 12% of oxygen feed is converted to CO ₂ , along with 4% to CO. ⁸ Soybean oil: 15% of oxygen feed is converted to CO and CO ₂ . ⁹ Pyrolysis oil: Generates more CO than CO ₂ . ³ Approximately 22% of the inlet oxygen is converted to CO and CO ₂ . ⁹
LPG bulk composition	–	–	Vegetable oil: LPG yield was the same as from VGO. ¹⁰ Pyrolysis oil: LPG yield decreased vs. VGO. ³
LPG trace composition	–	–	Ketones, aldehydes, carboxylic acids and furans. ¹¹ On some sites, levels of oxygenates in the LPG have increased by an order of magnitude (e.g., from 100 ppmv to 1,000 ppmv).
Amine acid gas (AAG) to the sulfur plant	A 0.65 mol%–0.8 mol% increase in the CO ₂ in AAG per 1% of coprocessed feed. This comes mostly from increased generation of CO ₂ from the biofeed, which outweighs the dilution effect from reducing the crude oil volume.	Acid gas from a dedicated HVO amine circuit would be predominantly CO ₂ with little H ₂ S. If there is not a pre-existing sulfur plant in the complex, then often a scavenger technology will be used to remove the H ₂ S. Some facilities run this through an additional amine unit designed to separate the H ₂ S and CO ₂ .	Increased CO ₂ , decreased H ₂ S vs. crude-only feed.
Sour water acid gas (SWAG) to the sulfur plant	Similar to AAG; 0.65 mol%–0.8 mol% increase in the CO ₂ in SWAG per 1% of coprocessed feed.	A 40%–50% increase in SWAG volume. CO ₂ content in combined SWAG increased to between 9%–22%, with the balance of composition being mostly hydrocarbons, hydrogen and nitrogen.	Increased CO ₂ , decreased H ₂ S and NH ₃ vs. crude-only feed.

comparable increase in CO₂ content in the amine acid gas to be processed in the SRU. Being a stronger acid than H₂S, CO₂ also requires more regeneration energy to strip from the solvent in the regenerator.

This extra duty load on the reboiler can potentially adversely affect the H₂S lean loading needed to meet product specification from the absorbers in the process loop. If the plant is already reboiler-limited, the quantity of coprocessed biofeed may need to be reduced.

If the plant uses a selective amine, such as methyl diethanolamine (MDEA), it has the potential to slip some of the extra CO₂ (since CO₂ can pass directly through the contactor without being removed), so that the effect of the extra CO₂ on the acid gas quality is not as significant as with non-selective amines. In some instances, it may be beneficial for an oil refinery to switch from ethanolamine (MEA), diethanolamine (DEA) or diglycolamine (DGA) to MDEA to offset the additional CO₂ and reduce energy consumption. However, it is more challenging for a weaker base like MDEA to meet treated

gas specifications at low pressure than it is for primary and secondary amines. MDEA also has a higher hydrocarbon solubility than MEA, DEA or DGA and is more vulnerable to foaming as a result.

The presence of the extra CO₂ in the rich solvent can accelerate corrosion in the bottom of the regenerator and reboiler if the steam flow up the regenerator column is not optimized for the extra duty (**FIG. 4**). Higher CO₂ loadings can increase

the risk of corrosion throughout the system. A detailed description of the mechanisms for this is provided in literature.¹²

In addition to CO₂, CO will also increase in the feed gases to the amine system because of coprocessing. CO is known to react with MDEA and caustic solutions to form formate salts¹³, while CO reacts with primary amines (MEA and DGA) or secondary amines (DEA and DIPA) to form formamides and for-

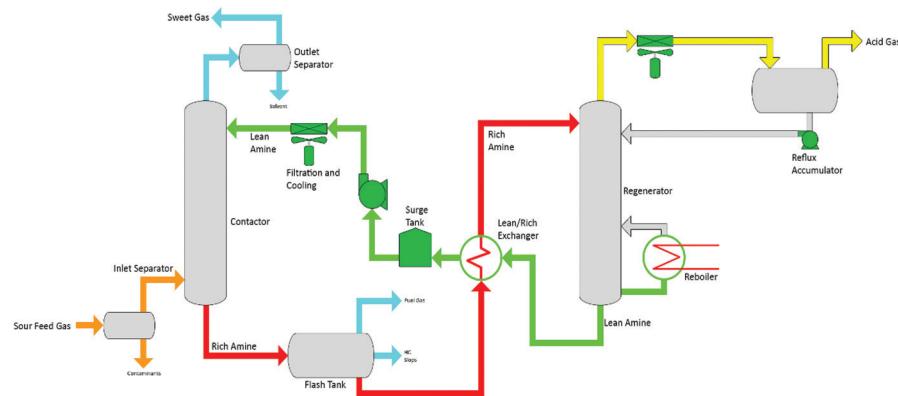


FIG. 3. Simplified amine system diagram.

mate salts. Formates have been shown to be corrosive to carbon steel in liquid and vapor states. Formamides do not appear to be corrosive, but they do increase viscosity and reduce amine available for acid gas removal.¹³

Field test results from several facilities coprocessing biofeed in their DHT showed an increase in CO in the hydrogen gas being amine treated from zero to the order of 1,500 ppmv–4,500 ppmv, with one facility showing a CO content of more than 10,000 ppmv. Therefore, the partial pressure of CO in the amine unit will normally be less than 100 kPa with current coprocessing levels. Based on observations in synthesis gas-treating amine systems, significant formate forma-



FIG. 4. Examples of corrosion caused by excessive CO₂ in various locations of an amine unit.

tion from CO does not normally occur at partial pressures less than 400 kPa.

Current biodiesel feedstocks contain large quantities of long-chain fatty acids. In their unprocessed form, these will have a major negative impact on the surface tension and viscosity of an amine solvent. In turn, this may cause the amine solvent to foam (or emulsify in the case of LPG treating). Conventional silicon and poly-glycol anti-foams have had some success in mitigation of this foam.

The FCCU biofeedstock coprocessing route appears especially vulnerable to foaming and emulsification problems. The authors are aware of five refineries coprocessing biofeedstock in their FCCUs, four of which experienced significant LPG emulsion issues as a result. Unlike the other two routes where hydrotreating is employed, there are many potential breakdown products that can be formed from catalytically cracking biofeedstocks. A summary of these is presented in **TABLE 3**. Tests on extracted phases of sour FCCU LPG have also indicated that high-oxygen content polymers may be present in the LPG.

Dealing with the emulsified FCCU LPG is a challenge, and conventional

techniques (anti-foams and carbon beds) do not appear to be adequate. Tailored demulsifiers injected into the sour LPG feeding the column have shown some success at reducing the emulsification; however, this treats the symptoms rather than removing the cause. Some success has also been achieved using proprietary absorbents on the LPG and the amine sides. In practice, a combination of absorbents and demulsifiers on the FCCU LPG treater seems to be required to achieve FCCU biofeed coprocessing blends of more than a few percent.

Impacts on sour water stripping.

Refinery biodiesel production often results in a significant increase in sour water volume as a result of the deoxygenation of biofeed with hydrogen and the water emulsified with the biofeedstock. The extra water may require debottlenecking of the sour water system or the installation of additional stripping capacity. The optimal strategy for debottlenecking is plant-specific and dependent on the pre-existing system. A holistic approach to the review of the complete refinery water system may reveal an opportunity to substantially reduce the use of fresh water.

A good process water strategy can have the following additional benefits:

- Reduced phenols in refinery effluent water
- Reduced fractionator overhead corrosion or less corrosion inhibitor use
- Reduced sodium in residue feeds, which may enable longer thermal cracker unit runs
- Reduced desalter emulsion issues

TABLE 3. Fatty acids known to be present in vegetable oils, and their FCCU breakdown products

Fatty acids in vegetable oil	FCCU breakdown products (fatty acids and triglycerides)
Lauric, myristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, erucic, hexadecenoic, arachidic, eicosenoic, behenic, docosadienoic and lignoceric	Methanol, ethanol, propanol, butanol, formic acid, acetic acid, propionic acid, butanoic acid, acetone, formaldehyde, acetaldehyde, acrylaldehyde, ethers, cyclic species, cresols, phenols, substituted morpholines and indoles

Note: A significant amount of the information in this table was provided by MPR Services

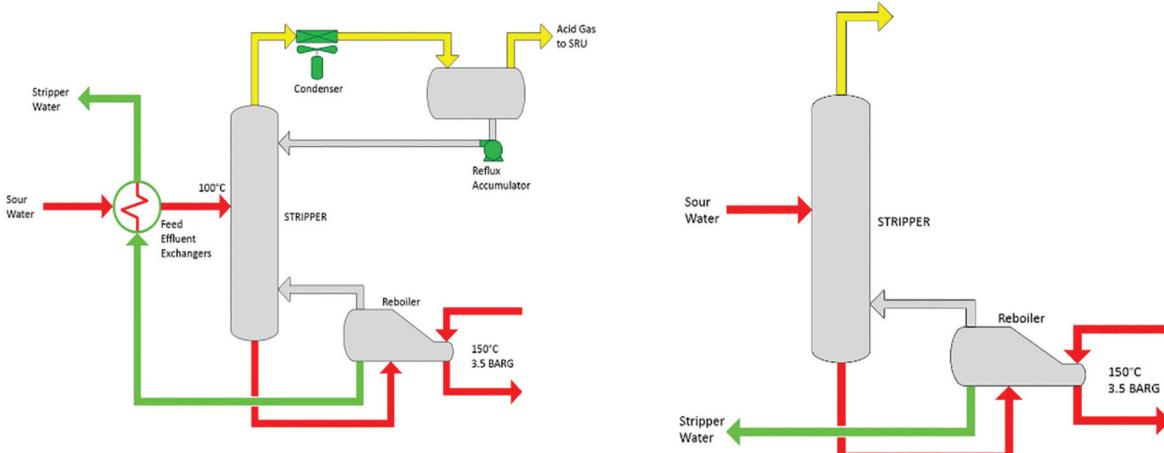


FIG. 5. A conventional SWS design (left) compared to the Lieberman low-CAPEX SWS design (right).

- Some spent caustic wastes could be neutralized in the sour water system.

With biodiesel production, the combined refinery sour water will contain more CO₂ and less H₂S and NH₃. There will also be a dilution effect because of the additional water produced. Consequently, more energy will be required to process wastewater generated from the biofeedstock, predominantly to increase the temperature of the extra water to stripping conditions. In most cases, the energy source is low-pressure steam, which is abundant in many facilities; however, the energy cost of stripping the wastewater should not be neglected when measuring the global benefits of a biodiesel project.

The co-authors' company has found the following steps to be effective in optimizing refinery water systems:

1. Perform a detailed compositional analysis of the refinery process unit water streams feeding the existing SWS system and their actual or estimated flowrates.
2. Estimate increased water volume and its CO₂ content based on biofeedstock properties.
3. Route streams with less than 10 mg/l H₂S and 50 mg/l NH₃ directly to final effluent treating to free up stripping capacity. While, in theory, these streams can be reused, often the hydrocarbon content and water hardness render them unsuitable.
4. With multiple SWSs, segregate phenolic waters and recycle them to the desalter. In the desalter, most of the phenol will be extracted back into the crude oil where it can subsequently be broken down in downstream hydrotreating.
5. Supplement desalter water with unstripped water from the crude overhead if capacity allows.
6. Use water streams with few strong cations and anions (e.g., some tail gas unit quench towers) as amine system makeup water.
7. Utilize a semi-stripped stream drawn from near the bottom of the SWS column (with approximately 200 ppmw NH₃) to potentially replace neutralizing chemicals injected into fractionator overheads for the desired pH of about 6.5, which saves on

8. Maximize the reuse of water from the low-pressure to high-pressure side on an FCCU, while not exceeding 25 ppmw hydrogen cyanide (HCN) and 2 wt% ammonium hydrosulfide (NH₄HS) in the high-pressure wash water.
9. **Note:** In-situ sulfidic spent caustic neutralization in an SWS is possible, but good pH control is essential and recycling sodium-containing stripped water upstream can have a negative effect on desalter performance (increased emulsification), thermal cracker time between decoking and FCCU catalyst life. Careful study is needed before doing this.

In many instances, the additional water from biodiesel production will require an additional SWS unit. The optimal process location for this is not necessarily far from this new water but will be site-specific. For instance, if there is not a pre-existing segregated phenolic water system, this may be the opportunity to install one on the catalytic and thermal cracking units, which are the source of phenols in the refinery water. This can save OPEX on expensive phenolic treatment of the water.

A new stripper also does not have to follow a conventional design. A stripper requiring a low capital expenditure (CAPEX), proposed by Lieberman, sends the hot stripped water directly to the plant desalter and can incur less than half of the final installed cost of a conventional unit (FIG. 5).¹⁴ This low-cost stripper does have some limitations, the

most significant being its sensitivity to reboiler duty. In one study, a 2% increase in reboiler duty increased SWS acid gas volume by about 30% (from water additional vapor), which can be a challenge for the SRU. This configuration works best when the low-CAPEX style stripper is contributing a relatively small proportion to the combined amine and sour water acid gases, and when the SRU is operating at a healthy load. This may not be suitable for facilities with a small ratio of amine acid gas (AAG) to sour water acid gas (SWAG); therefore, it is critical to confirm the SRU minimum turndown and to review burner controls.

There is often a range of trace-level strong ions in the various feed water sources to the sour water system. In conventional refining, these are normally sodium, chloride, sulfate and short-chain organic acids. Phosphate is present in most biofeedstocks, and, while pretreatment of biofeedstock will remove the bulk of the phosphate, trace amounts will emerge in the wastewater. While the concentration of these trace ions is usually small (< 500 mg/l), they can pose a significant operational challenge, as they will form an ionic bond with H₂S or NH₃ that renders them unstrippable at conventional SWS con-



FIG. 6. Raw sour water samples from various refinery units.

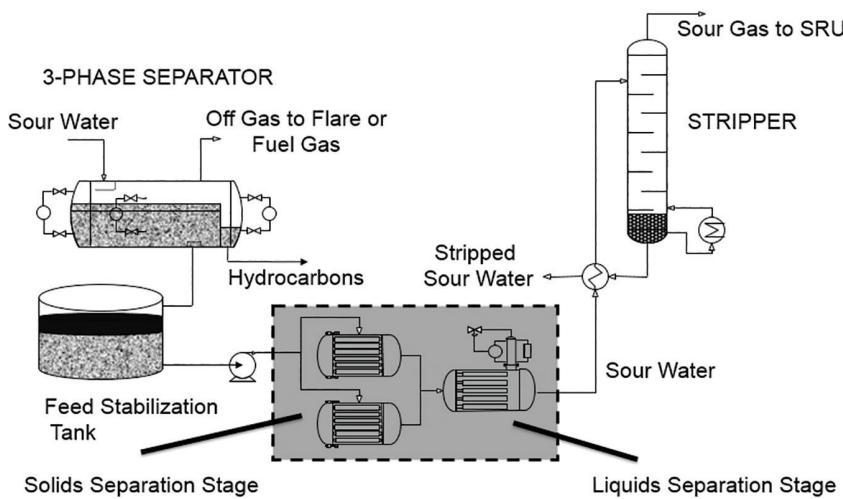


FIG. 7. Optimal wastewater filtration and coalescing scheme.¹⁶

ditions. Counter-dosing with an acid or base to neutralize them is common practice. Judicious addition of base in the optimal location can also reduce the energy requirements for stripping the water. Detailed discussions of this and other operational challenges in sour water stripping have been published in literature.¹⁵

Wastewater can also contain significant quantities of hydrocarbons and particulates, and may vary significantly in appearance, depending on the degree of contamination in the source waters (**FIG. 6**). Hydrocarbons that are not stripped from the water will often—in conjunction with particulates—form a fouling material that adversely affects SWS performance.¹⁵

In addition, lighter hydrocarbons that enter the SWS will be removed and sent with the overhead gas to the SRU. This may create operational problems for the SRU and be detrimental to its performance. Even a small increase in heavier hydrocarbons in the SWAG can result in a large increase in the amount of air required for combustion in the SRU reaction furnace, a phenomenon that is aggravated when the hydrocarbon content of the water is not stable. The following may occur in the SRU because of hydrocarbons in the sour water:

- Decreased hydraulic capacity
- Unstable plant operation due to variable air demand
- Damage to the SRU reaction furnace caused by rapid temperature variations
- Reduced efficiency because of poor H₂S-to-SO₂ ratio control
- Decreased recovery efficiency due to increased carbon disulfide (CS₂) formation
- Increased operating pressure from catalyst bed plugging by soot deposition from incomplete hydrocarbon combustion
- Decreased catalyst activity because of catalyst blockage from aromatic cracking
- Reduced sulfur quality due to soot in the sulfur product, resulting in “black sulfur”
- Soot fouling of the sulfur plant waste heat boiler and condenser systems.

These effects are extensively documented in literature.¹⁶

Hydrocarbons in water streams can be present in three forms: free, dissolved and emulsified.¹⁷ In most cases, biofeed co-

processing is done without resizing water separation vessels on the FCCU or HDT, which means less residence time for water and liquid hydrocarbon separation because of the increased water volume associated with processing biofeeds. Additionally, less time for separation can leave more liquid hydrocarbon in the wastewater from the FCCU or HDT.

Minimizing the hydrocarbon content of the sour water feed may be achieved by the following actions:

- Removing free hydrocarbons in the inlet three-phase separator; in general, 25 min of residence time with a liquid level at 50%–60% of drum height is optimal
- Installing a sufficiently large feed stabilization tank with hydrocarbon skimming facilities (sometimes, these tanks have several days of residence time, during which some emulsified hydrocarbons will come out of emulsion and may be removed)
- Installing a coalescer to remove emulsified hydrocarbons—typically, this requires pre-filters (**FIG. 7**)
- Using a hydro-cyclone separator to reject a hydrocarbon-rich light phase back to the feed stabilization tank.

Part 2. Part 2 will be published in the February issue. **HP**

NOTES

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Maximize value and successfully revamp a fired heater

Fired heaters are facing scrutiny because they contribute to the global emissions of carbon dioxide (CO_2) and nitrogen oxides (NO_x). For refineries and petrochemical plants focused on reducing greenhouse gas (GHG) emissions, it makes sense to target CO_2 from fired heaters, since they usually have a fuel efficiency of 70%–90% and are a major contributor of the site's overall emissions production. However, revamping fired heaters only to reduce emissions, whether for NO_x or CO_2 , is unattractive for operators, as it does not generate additional value.

A revamp that improves heater capacity, reliability and availability creates much more value. Revamping a fired heater can be a complex task, especially when dealing with multiple problems simultaneously. A structured methodology is required to successfully determine what problems must be resolved, in what priority, and what decisions must be made to determine the best possible solution.

An example of a successful revamp using this methodology will be used to demonstrate that the goal of emissions reductions can be achieved while improving the bottom line.

ELEMENTS OF A SUCCESSFUL REVAMP

The Kepner-Tregoe matrix is ideal for analyzing a complex revamp and consists of four approaches:

1. Situational analysis: A high-level definition of the concerns to address
2. Problem analysis: Narrowing in on the specifics and determining root causes
3. Decision analysis: Collecting and evaluating alternatives

on the merits and risks, and deciding which option is the best possible choice

4. Potential problem analysis: A preventative step to evaluate the impact of the decisions on the system and avoid new problems.

These approaches are demonstrated for a recent retrofit of a vertical cylindrical heater by the author's company.

Situation analysis. This approach is usually performed by the owner-operator. In this example, the high-level issue for the owner was the heater capacity. A plant study showed that the output could be increased by 20%–30% if the crude heater could be debottlenecked. However, secondary issues also had to be

resolved before a capacity increase could even be considered. The most obvious was that many radiant tubes showed damage, such as high-temperature oxidation, tube wall thinning and creep. Another concern was the brief time between coke cycles, indicative of a potentially high coking rate. Any solutions must consider stringent NO_x emissions limits as well as high CO_2 taxes that would be imposed after the year 2020.

Problem analysis. Fired heaters are complex pieces of equipment that can be difficult to analyze. The key to a successful retrofit begins with an engineering study to understand all aspects of the heater. Most heater studies begin with a survey in the field to record the present mechanical condition of the heater,



FIG. 1. Rolling flames.

observe the flames, measure stack emissions and collect operating data. This is also an excellent opportunity to interview operators about difficulties they experience controlling the heater. This information is used to generate thermo-hydraulic models to identify bottlenecks in present or future operations. Comparing the model results with actual operating data can reveal issues that are not readily observed, like fouling inside the tubes or loss of heat transfer in the convection section.

Key findings of the survey of the VC heater included:

- Temperature/heat flux

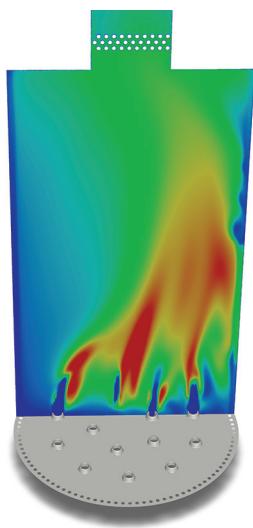


FIG. 2. Temperature contours on the center plane of the VC heater.

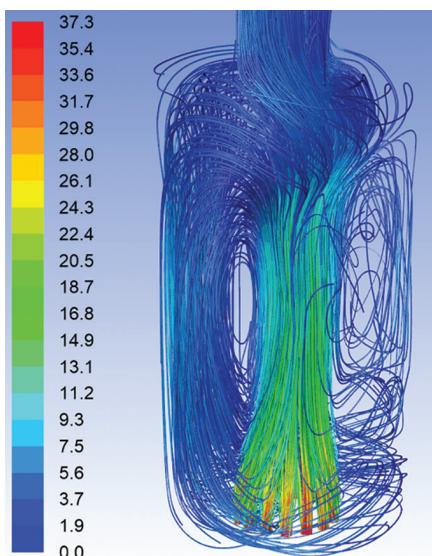


FIG. 3. Streamlines of the optimized burner circle with 15 burners.

maldistribution. The peak skin temperature difference between the hottest and coldest pass was $\sim 50^{\circ}\text{C}$ ($\sim 90^{\circ}\text{F}$) at start-of-run (SOR). This imbalance increased to about 150°C (270°F) at end-of-run (EOR).

- **Short run length.** The radiant tube skin temperatures increased by $\sim 120^{\circ}\text{C}$ ($\sim 216^{\circ}\text{F}$) in only 3 mos.
- **Low fuel efficiency.** The field data indicated an efficiency between 78% and 79%, despite good mechanical condition of the heater and efficient operation of the burners.
- **Loss of heat transfer.** Comparison with the thermal models showed that the actual fuel efficiency at SOR (i.e., in clean condition) should have been 2% higher.

Visual observation of the firebox showed flame interactions, which almost always result in a performance penalty. Flames rolling into tubes (FIG. 1) cause hotspots, excessive coke formation, oxidation and tube damage from oxidation, creep and carburization. Unruly flames are a safety concern, produce high emissions and shorten the life of many components.

The root cause of the flame interactions was investigated by a computational fluid dynamics (CFD) analysis of the heater. CFD is a common tool to evaluate the performance before and after a fired heater revamp (FIG. 2).

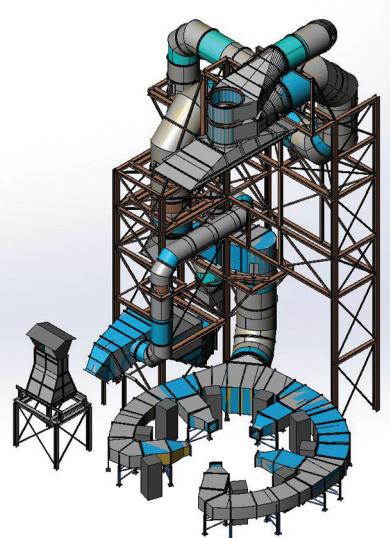


FIG. 4. Overview of revamp scope.

In the original design of the firebox, the natural draft burners were arranged in two circles. The outer ring consisted of 10 burners while the inner ring consisted of five burners. This layout caused poor flue gas recirculation patterns and flames coalescing in an unsteady flame cloud. Additionally, the outer burners were too close to the radiant tubes, causing flames to locally impinge, creating hotspots. The CFD model replicated the poor flame patterns and explained the difference in coil temperatures, high coking rates and tube degradation issues.

Decision analysis. Armed with information from an engineering study and CFD analysis, the contractor and the operator jointly evaluate the potential revamp opportunities to reach an achievable and optimal retrofit target. For a heater revamp, these include (but are not limited to):

- Improve safety, reliability and operability
 - Eliminate flame interaction problems
 - Simplify burner control
 - Eliminate ambient effects (e.g., wind, rain)
- Reduce operating costs
 - Increase fuel efficiency
 - Reduce fouling in tubes
- Increase profitability
 - Increase capacity and throughput
 - Switch to more economic fuels or feedstocks
- Reduce emissions
 - NO_x
 - Greenhouse gases (CO_2)
 - Unburned hydrocarbons [carbon monoxide (CO), CxHy]

Ideally, several scenarios are developed, including estimates for CAPEX and OPEX, while considering credits or penalties for CO_2 emissions. For this example, the following solutions were considered, also shown in TABLE 1.

Option 1: Change existing burner layout. Since flame impingement is a crucial factor in operational and reliability issues of the heater, the author's company investigated whether moving the natural draft burners to a single burner circle would improve the overall flame performance. This optimization can be difficult since moving the burners farther from the radiant coils puts them

closer together, which increases the risk of flame-flame interactions. Several CFD iterations were used to determine the optimal burner circle diameter (**FIG. 3**). In this scenario, some interactions are still apparent, causing the flames to lean slightly to the center. Nonetheless, the new layout produced an acceptable flame pattern and flux profile. The improved flux profile resulted in improved heat flux and temperature uniformity, allowing the heater to operate at greater capacity. Since neither the burner liberation rate nor the heater surface area increased, this capacity increase is limited. Absence of flame interactions will reduce NO_x emissions. This solution requires a new heater floor.

Option 2: Convection replacement. Replacing the damaged/fouled convection section with a new and more efficient version would increase the fuel efficiency by several percentage points. However, with a feed inlet temperature range of 170°C–200°C (338°F–392°F), the minimum achievable stack temperature is ~250°C (~482°F), which limits the fuel efficiency to a maximum of 86%. The 8% gain could lower fuel consumption and CO₂ emissions or increase the heater capacity. This option does not address the flame interference problems, so it also requires Option 1 or 3 to de-constrain the firebox operation.

Option 3: Forced-draft air reheat (FDAPH). The stack temperature of a heater with 78% fuel efficiency is ~400°C (~750°F). This heat can be used to heat the combustion air to 300°C–350°C (572°F–662°F). More heat can be extracted from the flue gas than in Option 2, pushing fuel efficiency to more than 90%. The maximum efficiency is only limited by the dewpoint of sulfuric acid, which, in this case, restricts the stack temperature to a minimum of 165°C (329°F).

In this case, the burners must be replaced with forced-draft type burners, which have a few advantages:

- The burner capacity can be drastically increased, which allows the number of burners to be reduced from 15 to five. This allows the use of the inner burner circle without making major modifications to the heater floor other than plugging the outer ring of burners.

- The high air side pressure drop of forced-draft (FD) burners results in a more compact and robust flame, which provides more freedom in locating them without causing flame interaction problems.
- FD burners are not individually controlled by air dampers, but by the FD fan damper or variable speed motor, which simplifies the operator's job.
- FD burners are not sensitive to ambient effects like wind or rain, which reduces the variability in firebox draft and oxygen. This allows the heater to be operated more consistently and on less excess air, which further improves the system efficiency.

The scope of this option is more substantial than the others, resulting in the highest overall CAPEX:

- New FD burners and pilots
- Fuel piping
- Flue gas/air exchangers
- FD and ID fans with variable-speed drives
- Flue gas and air ducting with structural support
- New transition duct and bypass dampers.

While Option 2 (convection replacement) showed the quickest payback

time, it only made sense in combination with Option 1 or Option 3, which reduced the economic feasibility. Also, the combination of Options 1 and 2 would not allow for the capacity increase that the customer desired.

Option 3 showed the biggest benefits and the most attractive economics. Purely based on fuel savings and CO₂ tax

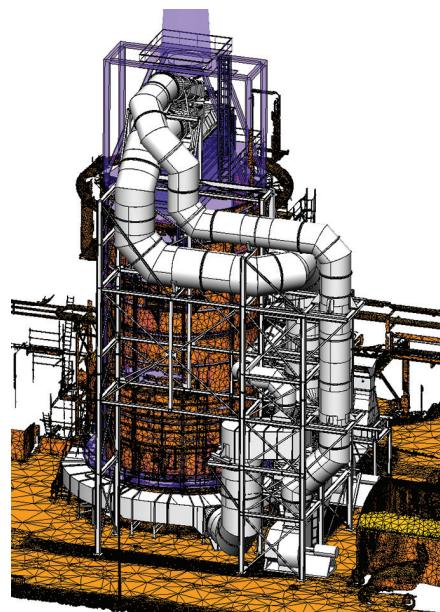


FIG. 6. Model from laser scan (shown as mesh) integrated with new equipment (shown in grey).

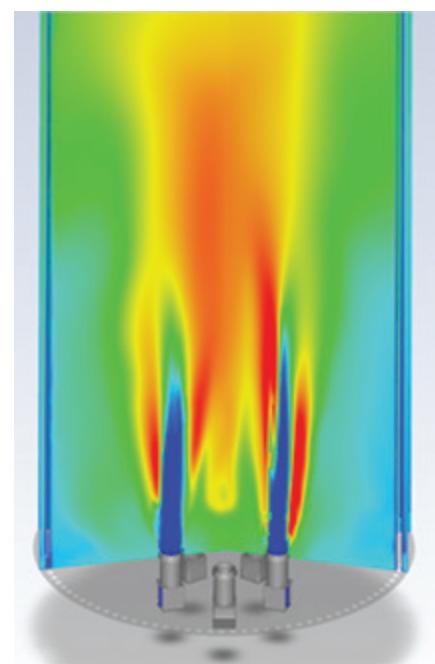


FIG. 5. Temperature contours with five FD burners.



FIG. 7. Model of revamped heater.

TABLE 1. Four potential solutions

	Change existing burner layout	Convection replacement	FD APH	Do nothing
Flame interaction	+	0	+++	---
Simplify operation	0	0	++	0
Eliminate ambient effects	0	0	+++	0
Increase fuel efficiency	0	++	+++	0
Reduce fouling	++	++	+++	-
Increase capacity	+	++	+++	-
Reduce emissions	+	+	+	0
CAPEX	-	--	---	0
OPEX	0	+++	++	0
Implementation time	-	--	-	0

**FIG. 8.** Flames after revamp.

avoidance, the project showed a payback period of less than 2 yr. Most importantly, this option allowed for the highest capacity increase (29%). One benefit of this option was that a substantial portion of the work could be done with the heater in operation, reducing downtime. An overview of the revamp scope is shown in **FIG. 4**.

Potential problem analysis. A drastic modification like this can result in unforeseen issues. Importantly, during the change of the combustion system and air supply, potential issues include:

- Flame shape, flame interactions, NO_x emissions, incident radiant flux profile, and temperature uniformity using five high-capacity

FDAPH burners

- Air distribution inside the new combustion air duct
- APH bypass duct design to prevent acid dewpoint corrosion.

To mitigate the impact on NO_x and ensure the best possible flame performance, an innovative company^a designed the burners. They selected a proprietary round flame burner^b for its compact design and its ability to produce very low NO_x emissions while meeting the flux profile requirements for this project for a wide fuel composition ranging from natural gas to liquefied petroleum gas (LPG). Despite the much higher heat release and air temperature, the burner^b fit in the existing openings of the ND burner, so no floor modifications were necessary. A CFD model of the new arrangement (**FIG. 5**) demonstrated that flame impingement would be eliminated with the proposed arrangement while meeting NO_x requirements.

On the execution side, a risk that required mitigation was the potential interference of the large APH structure with the existing equipment. The heater and its surrounding area were scanned using lasers, which produced a 3D model that was imported into the author's company's model. During construction, the distance between the new and existing equipment was as small as 0.5 in. Thanks to the laser scan technology and 3D modeling (**FIG. 6**), zero field interferences or fit-up issues were experienced.

Results. The turnkey project was successfully executed within 7 mos from

placement of purchase order to startup. By following a structured decision methodology like the Kepner-Tregoe Matrix, the optimal solution was selected considering CAPEX, OPEX, process availability, reliability and plant throughput. Integration of smart tools like CFD and 3D modeling in every facet of the design process prevents mistakes and rework while ensuring the project goals are met (**FIG. 7**). The burners^b produce well-behaved flames without visible interactions (**FIG. 8**). Due to the solid improvement in heat flux uniformity, the coil outlet temperatures are now within a narrow band. The fuel efficiency and capacity goals were met while peak skin temperatures at SOR were 100°C lower than before the revamp. The predicted NO_x emissions from the CFD model were validated with official stack measurements, which showed that the actual emissions were 30% below the required limits. **HP**

NOTES

^a Broken Arrow-based company, Zeeco

^b GLSF FREE JET round flame burner



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Gas-side fouling effects on transfer-line exchangers

Transfer-line exchangers (TLEs) are specific shell-and-tube heat exchangers installed out of hydrocarbons steam cracking furnaces for olefins production. Their purpose is to cool process gas coming from the furnace with a minimum residence time—TLEs are also known as quenchers. The quenching is achieved by means of high-pressure vaporizing water as cooling fluid, flowing on the shell side. Up to three TLEs in series can be installed downstream of a furnace coil, depending on the process and feedstock. The first one of the series, called the primary TLE (**FIG. 1**), is the most critical from an operating and thermal-mechanical standpoint due to harsh operating conditions.

Gas-side fouling in a TLE is a major source of operating and maintenance issues; chiefly, massive deposits of tar and coke on the internal surface of tubes lead to a rapid degradation of quenching. It then becomes vital to perform frequent cleaning operations with a consequent loss of production yield. This article focuses on gas-side fouling effects and consequential potential issues that are not well known or that are sometimes intentionally or unintentionally overlooked. A proper and exhaustive understanding of fouling consequences on quenching can help to extend the design life of a TLE and reduce annoying and costly operations, such as repairs. The information presented here is based on the author's company's knowledge and experience as a global supplier of a proprietary design TLE, but these concepts can be extended to any other TLE design.

Fouling in TLE. Heat transfer resistance in the primary TLE due to gas-side fouling is one of the largest incidences in heat transfer technology for the petrochemical industry, since it can reach (before cleaning) values of $0.001 \text{ m}^2\text{C}/\text{W}$ – $0.005 \text{ m}^2\text{C}/\text{W}$. It is even more remarkable that such foul-

ing levels can be reached, from clean conditions, in 40 d–60 d of operations.

Of course, fouling is experienced as well in the upstream furnace coil, even at higher levels. Practically, operations and plant production yield are strongly linked to gas-side fouling effects. For this reason, several attempts to catalogue feedstocks in terms of fouling source, to understand mechanisms of fouling growth, and to introduce techniques or solutions to mitigate fouling deposition have been proposed.

According to literature, the type and amount of gas-side fouling mainly depend on furnace feedstock and cracking operating parameters. Furnace feedstock can be either gaseous (ethane to butane) or liquid (naphtha to gasoil) hydrocarbons—it is generally understood that fouling in TLEs is a consequence of the formation of coke and tars and, more specifically, that gaseous cracking mainly promotes fouling growth at the TLE inlet, whereas liquid cracking mainly promotes fouling growth along the tube length. The author, according to feedback received from operating units based on different processes, agrees with such a general understanding, although (1) observations are generally done after on-line cleaning so there is not a direct picture of fouling, and (2) no clear observations can be obtained when mixed cracking is performed.

Among operating parameters, the cracked gas temperature and velocity, the tube metal temperature and surface roughness play a role in fouling growth. From a thermodynamics and kinetics standpoint, two major root mechanisms are deemed responsible for gas-side fouling formation:

1. Catalytic reactions on the metallic surface of the TLE tube forming coke and tar compounds directly on the tube surface¹
2. Polymerization reactions in the bulk of gas forming coke

and tar compounds, which impinge or migrate towards the TLE tube surface and then condense and stick.²

The first mechanism is likely promoted on the hottest metallic surfaces (at the inlet of the TLE) and at startup (clean surfaces), whereas the second mechanism is likely promoted by the presence of local turbulence and/or colder metallic surfaces (along the tube length). Models of fouling formation and deposition in TLE tubes are available in literature.³

However, possible fluctuations in chemical composition and temperature of cracked gas, turbulence in the TLE inlet channel, and flowrate unbalance between tubes can all introduce a stochastic contribution to the fouling deposition and growth at the TLE inlet. In practice, this

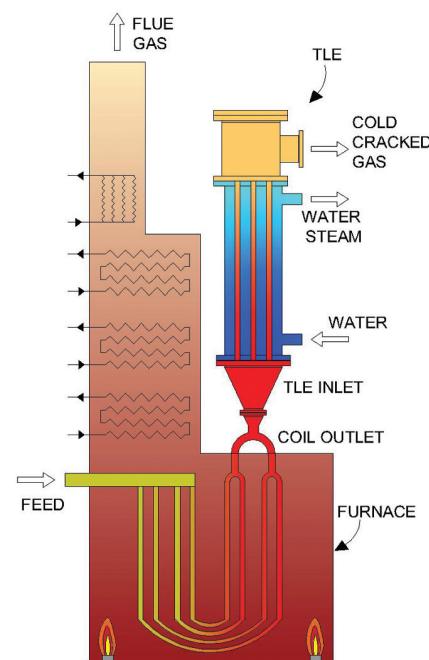


FIG. 1. TLEs are specific shell-and-tube heat exchangers designed to cool process gas coming from the furnace with a minimum residence time.

is impossible to be exhaustively predicted; moreover, the cracked gas at high velocity can also strip off fouling from the furnace coil and bring it to the TLE inlet. This is corroborated by the fact that fouling deposition at the tubes inlet is not uniform and can even change between subsequent inspections—the position and number of clogged tubes at the inlet appear to be stochastic rather than deterministic. Accordingly, the author thinks that turbulence and back-mixing at the tubes inlet first led to localized tiny layers or spots of fouling that act as a substrate for further fouling sticking and the possible clogging of tubes.

Contrary to the fouling deposited at tubes inlet, of which the extension and aspect appear stochastic, the fouling along the tube length appears more uniform, both from tube-to-tube and from run-to-run. Therefore, the fouling is more linked to deterministic phenomena or linked to a lesser number of concurrent phenomena; actually, along the tube, the gas path is more regular and the turbulence is smoother. Yet, quantitative measurements (thickness, morphology, etc.) would require samples collection along the tube.

FIG. 2 shows two examples of gas-side fouling after on-line cleaning of a TLE:

- **FIGS. 2A, 2B and 2C** refer to a TLE working with gaseous feedstock (propane/butane).

- **FIG. 2A** shows clogging in a tube, 60 mm–70 mm from the inlet.
- **FIG. 2B** shows residual fouling along the length of a tube.
- **FIG. 2C** shows an inlet tubesheet in clean condition except for some outer tubes that remain clogged.
- **FIG. 2D** shows a TLE working with liquid feedstock (heavy naphtha) during mechanical cleaning. Thick, compact and uniform fouling along the tube length is apparent; this TLE was difficult to mechanically clean due to hardened fouling along the tube length.
- **FIGS. 2A, 2B, 2C and 2D** indicate that on-line cleaning can be unsuccessful. **FIGS. 2A, 2B and 2C** indicate that some tubes are still clogged or contain residual fouling after on-line cleaning, whereas **FIG. 2D** indicates that fouling along the tube length leads to hardening and aging along runs.

TLE operations. The hot cracked gas is usually quenched in the primary TLE from 780°C–850°C to 350°C–600°C, depending on the process and feedstock. Typically, the gas temperature at the TLE outlet increases by 50°C–200°C due to fouling, then production operations are shut down and on-line/mechanical clean-

ing of equipment is undertaken. Due to complex thermodynamics and kinetics of steam cracking and to high fouling levels, a tight process control is inherently difficult. Gas temperature and feedstock conversion at the furnace coil outlet are major control parameters; the cracking furnace is also controlled by measuring the pressure of cracked gas at the inlet and/or outlet of the TLE and by measuring the temperature of cracked gas at the TLE outlet. Usually, production is halted and cleaning is performed as one of the following constraints due to fouling:

- The cracked gas pressure drop approaches the maximum allowable
- The cracked gas temperature at the TLE outlet approaches the maximum allowable
- The maximum coil metal temperature approaches the maximum allowable.

Pressure instruments can be installed either at the coil or TLE outlet, or both. In the first case (coil), the pressure drop across the cracking coil is accurately measured, whereas the pressure drop across the TLE can be overlooked if the downstream pressure measurement is far from the primary TLE. In the second case (TLE outlet), the overall pressure drops across the coil and TLE are accurately measured, but no clear indication exists about specific drops. Finally, an accurate and exhaustive valuation of pressure drops can be done if a two-points measurement—at both the coil and TLE outlet—is carried out.

However, latent and tricky problems may arise from typical furnace process control when run lengths are determined by TLE conditions. The pressure drop across the coil/TLE and the temperature of the cracked gas at the TLE outlet are often weakly coupled; usually, cleaning operation is decided once one of the two parameters (pressure drop, outlet temperature) approaches the relevant allowable limit, whichever occurs earlier without inferring on the other parameter. In other words, the following risky operating conditions may occur:

1. The pressure measured at the coil outlet is acceptable, the temperature measured at the TLE outlet is acceptable, and no accurate measurement for pressure at the TLE outlet is available. In this case, measurement of the TLE outlet

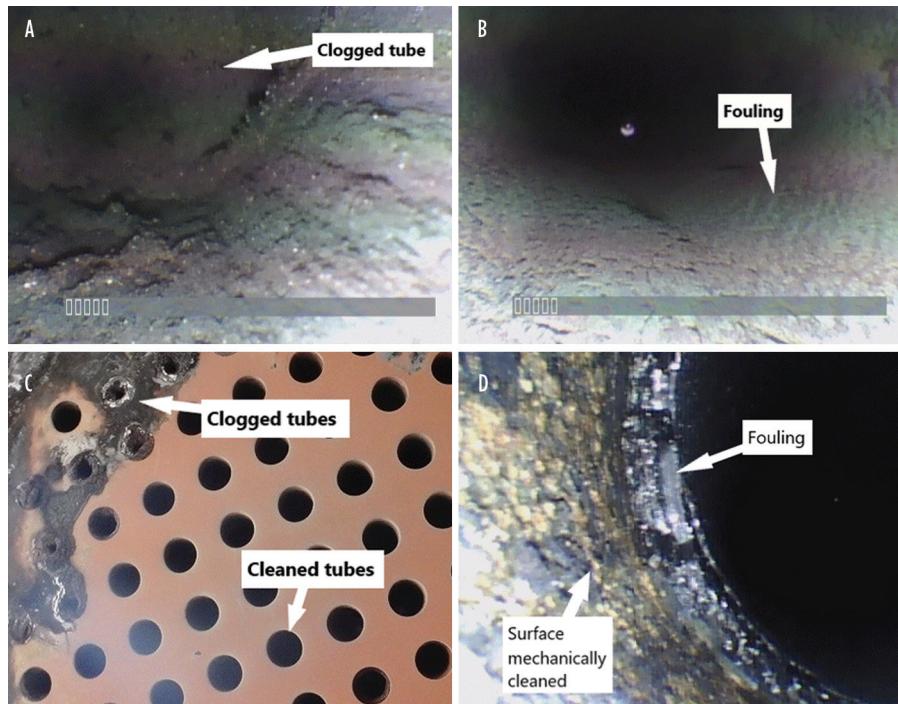


FIG. 2. Examples of gas-side fouling after on-line cleaning of a TLE.

temperature cannot truly give indications about fouling in the TLE and, more specifically, if the fouling is mostly deposited along the exchanging tubes or at the tubes entry. In other words, it is not possible to infer if the TLE tubes are all working with fouling spread along the tube length or if the TLE works with clogged tubes.

2. The pressure measured at the TLE outlet is acceptable, the temperature measured at the TLE outlet is acceptable, and no pressure measurement is available at the coil outlet. In this case, the overall pressure drops across the coil and the TLE can be within the allowable limit, but there is no clear indication how the pressure drop is distributed between the coil and the TLE. In other words, most of the pressure drop may occur across the TLE and, consequently, several tubes and/or inlet grids/shields may be clogged, leading to non-uniform distribution of gas in the TLE tubes and overloading some tubes.
3. The pressure measured at the coil outlet is acceptable, the temperature measured at the TLE outlet is acceptable, and the pressure measured at the TLE outlet is high or the pressure drop in the TLE increases faster than in the coil. In this case, the operating conditions of the coil and the TLE are known and acceptable since the sum of pressure drops across the coil and TLE is within the overall allowable limit. Therefore, rather than shutting down and cleaning the TLE, it may be decided to proceed with production and to use available pressure drop in the coil for the TLE. As a result, the TLE works with a high pressure drop, which could mean that several tubes are clogged.

For the above three operating conditions, the risk is represented by the overloading of the TLE tubes. When some tubes are clogged due to fouling growth at their inlet, the cracked gas (probably non-uniformly) distributes into the remaining tubes. Yet, the TLE outlet tem-

perature may stay below the allowable limit, since the tube bundle is provided with a heat transfer surface overdesign or because the remaining working tubes are clean or partially fouled. Because of thermal-hydraulics and thermal-mechanical design of the TLE are carried out considering all exchanging tubes in operation, a TLE with clogged tubes works outside its design conditions; consequently, the design life of the TLE can be jeopardized. It should be emphasized that, even if general observations indicate that fouling growth at tubes inlet is more pronounced for gaseous cracking furnaces, all TLEs are potentially exposed to tubes clogging since fouling at the TLE inlet is unpredictable.

TLE performance. Results of heat transfer performance calculations of a typical TLE are shown in FIGS. 3–6. The TLE is receiving gas from an ethane cracking furnace at 830°C and 205 kPa(a), and with a molecular weight of 18.7 kg/kmol. Nominal design of the TLE is made for an outlet gas temperature of 373°C and a pressure drop of 6 kPa, with water-side fouling resistance set to 0.000086 m²C/W and clean conditions on the gas side. Boiling water temperature is 325°C. Exchanging tubes are made of low-alloy steel and have outside and inside diameters of 50.8 mm and 40 mm, respectively. Tube length is 7.5 m.

The performance calculations are made for two boundary operating conditions:

1. Clean, which means fouling on the water side and no fouling on the gas side

2. Fouled, which means fouling on both sides, with gas-side fouling assumed to be uniformly distributed in tubes and along the tube length.

The maximum allowable outlet temperature for the cracked gas is 430°C: accordingly, all the calculations in fouled conditions are made in design mode by imposing a gas-side fouling coefficient that provides for an outlet gas temperature of 430°C.

In FIGS. 3–5, percentages in abscissas represent the number of TLE working tubes: 100% means that all TLE tubes are working, whereas 70% means that 30% of tubes are clogged by fouling and therefore do not contribute to heat exchange.

For FIGS. 4 and 5, it is assumed that, for fouled conditions, the gas-side fouling has no effect on gas pressure drop; in other words, FIGS. 4 and 5 show trends as if fouling has no thickness. Conversely, for FIG. 6, an imposed thickness for the gas-side fouling (in abscissas) has been considered for calculations, always according to the above assumption that fouling distribution in tubes and along tube length is uniform.

The following considerations can be drawn from the results of performance calculations:

- a. FIG. 3 illustrates the gas pressure drop and outlet temperature, in clean conditions, against the number of working tubes. The two quantities increase by increasing the number of clogged tubes exponentially. The pressure drop trend in case of fouled conditions—

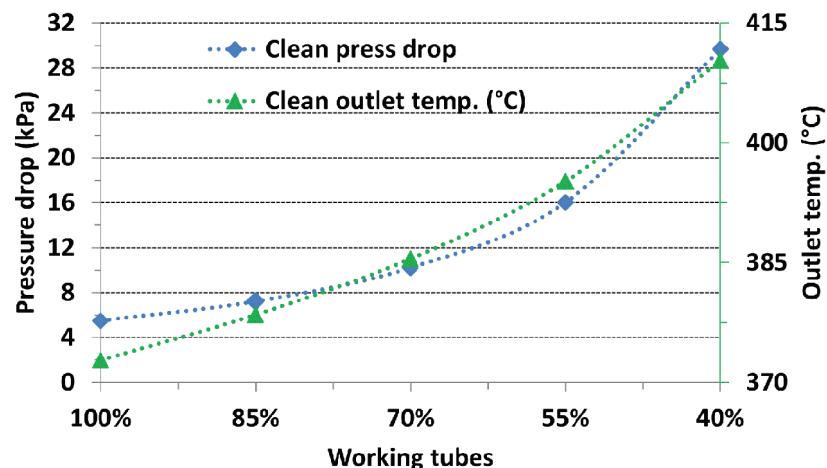


FIG. 3. The gas pressure drop and outlet temperature, in clean conditions, against the number of working tubes.

assuming zero thickness fouling—is like the clean one.

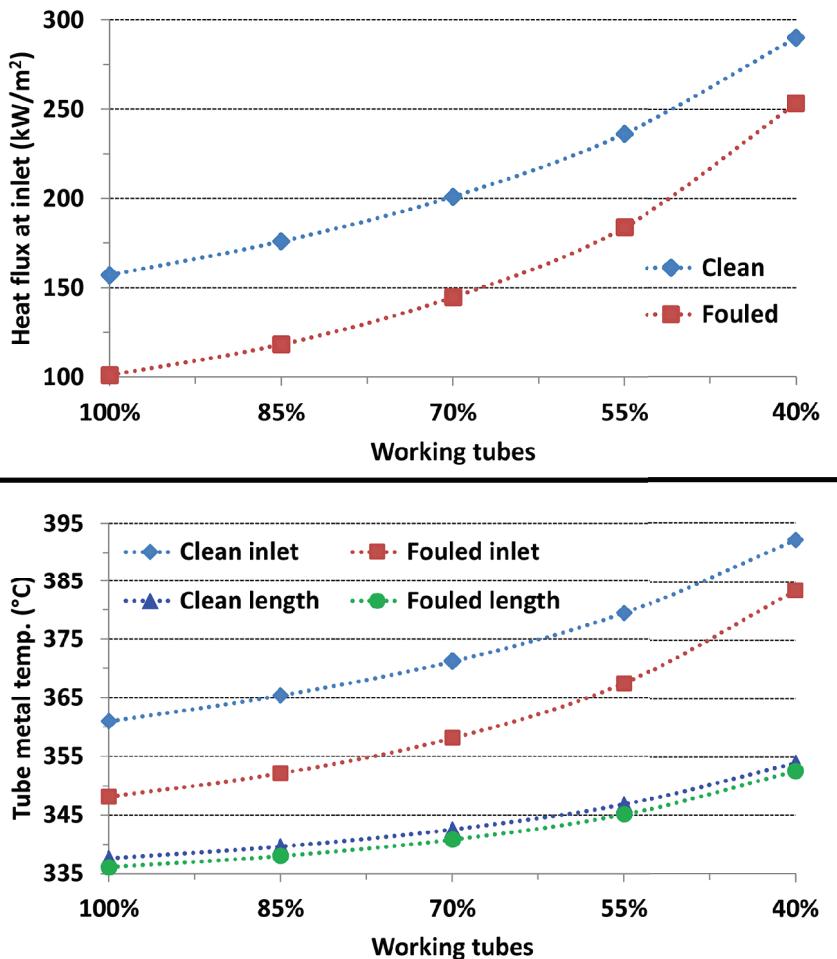
- b. FIGS. 4 and 5 show the heat flux at the tube inlet and the tube metal temperature (TMT), for fouled and clean conditions, against the number of working tubes. The TMT is given for the tube inlet, averaged across the tube thickness, and for tube length, averaged along the length and across the tube thickness. Trends in FIGS. 4 and 5 indicate that these parameters increase by increasing the number of clogged tubes, and that the increase becomes steeper.
- c. In FIGS. 4 and 5, it is apparent that fouling is “protecting” the tube from high gas temperature and heat flux. In other words:
 1. When several tubes are clogged, the remaining working tubes are cleaner and the conditions from a thermal-

hydraulics standpoint are more critical. At the tube inlet where the heat transfer is the most critical, the heat flux and the TMT of the working tubes increase with growing clogging; this can have consequences on boiling mechanism and cooling efficiency on the water side. It should be noted that, when several tubes are clogged, the working tubes are in overloaded conditions and are at risk of overheating and/or corrosion.

- d. In FIG. 5, the TMT averaged along the tube length and across the thickness increases with the number of clogged tubes. This has a consequence from a thermal-mechanical standpoint since tube buckling is intensified. It must be noted that clogged tubes are colder than working tubes, so differential thermal elongations may give

high local stresses, particularly at tube-to-tubesheet joints. Referring to tube buckling, FIG. 5 shows that again clean conditions (i.e., no fouling deposited along the tube length) can be more critical than fouled conditions since the TMT averaged along the tube length is higher for clean conditions.

- e. FIG. 6 shows trends of pressure drop (in ordinates) at different fouling thicknesses in tubes (in abscissas) and at a different percentage of clogged tubes. The nominal design pressure drop (6 kPa) is doubled or tripled if either heavy fouling deposition along the tube length (several millimetres of fouling thickness) or several clogged tubes—or both—occur. However, FIG. 6 also indicates that when pressure drop across the TLE rapidly rises, this is likely due to clogging of tubes rather than fouling deposition along the tube length. This must be considered because, if the pressure drop limit for cleaning operations is set at a high value, the TLE may work with a significant portion of clogged tubes, which means that the remaining working tubes are in overloaded conditions.
- f. FIG. 6 also indicates that when the gas-side fouling mainly occurs along the tube length, it is likely that the outlet gas temperature limit is reached before the outlet gas pressure limit. Conversely, when the gas-side fouling growth is more promoted at the inlet tubesheet and tube inlet (i.e., the fouling tends to clog the tubes), it is likely that the outlet gas pressure limit is reached before the outlet gas temperature limit.
- g. The outlet gas temperature trend in FIG. 3 and previous point (e) emphasize that:
 1. For the theoretical condition of nearly 50% of tubes clogged and 50% of tubes working and clean, the TLE would not reach the outlet gas temperature limit; however, the working tubes would be at 200% of load (overloaded conditions).
 2. When fouling growth is more promoted at the tube inlet



FIGS. 4 and 5. The heat flux at the tube inlet (top) and the tube metal temperature (bottom), for fouled and clean conditions, against the number of working tubes.

(clogging), the TLE should be shut down due to pressure drop limit rather than outlet gas temperature limit; yet, if the overall pressure drop across the coil and TLE is still acceptable, plant operators will likely continue running the furnace and, therefore, the TLE working tubes will be overloaded.

Additionally, gas velocity in tubes, chiefly at the inlet, increases proportionally with the number of clogged tubes, up to inadmissible values.

Suggestions and takeaways. The primary TLE installed in steam cracking furnaces suffers from heavy gas-side fouling: the formation and growth are governed by several parameters and indeterministic phenomena. Accordingly, operating runs and cleaning of the TLE should rely on plant operators' experience and observations. Regular inspections on the gas side can help clarify how a TLE is running and if on-line cleaning is effective. The author has noted that on-line cleaning is not always successful in unclogging the tubes and removing the fouling along the tube length. The following suggestions are for plant operators:

- Conduct gas-side inspections at least twice per year.
- Report the type and extension of fouling during gas-side inspections, specifying if a prior on-line cleaning has been done or not.
- Correlate different feedstocks and cracking severity with fouling type and extension.
- Consider installing a pressure measurement both at the coil and TLE outlets, if not yet implemented.
- A high pressure drop across the TLE due to tubes clogging is a risky and tricky condition—worse than heavy fouling spread along the tube length.
- When pressure drop across the TLE is rising fast, and is rising faster than the increase of the outlet gas temperature, it likely indicates that tube clogging is occurring.
- If gas-side inspections reveal that clogged tubes are present also after on-line cleaning of the TLE, consider starting on-line cleaning

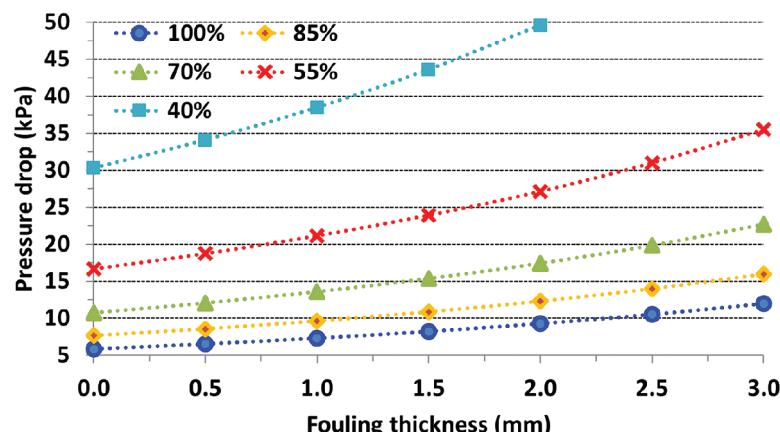


FIG. 6. Trends of pressure drop (in ordinates) at different fouling thicknesses in tubes (in abscissas) and at a different percentage of clogged tubes.

at relatively low pressure drop across the TLE (1.5–2 times the allowable one in clean conditions) provided that the gas outlet temperature is still acceptable.

- If gas-side inspections indicate that clogging of a tube inlet is not promoted or not important and the rise of pressure drop across the TLE is moderately slow, the cleaning of the TLE can be started at a higher pressure drop (3–4 times the allowable one in clean conditions) provided that the gas outlet temperature is still acceptable.
- If gas-side inspections indicate that clogging of the tube inlet is important and some tubes are even clogged after on-line cleaning, operators should decide for frequent mechanical cleaning, at least at each inspection. A TLE should not be re-started with clogged tubes.
- On-line cleaning of the TLE due to end-of-run (EOR) conditions (high pressure drop or high outlet temperature) should restore start-of-run (SOR) conditions—except for water-side fouling, which is, in any case, slow. Plant operators must assess if SOR conditions are efficiently restored (if feedstock has not been changed); if no, this means that the on-line cleaning has not been effective, and that the TLE is becoming more and more fouled, so a mechanical cleaning should be performed.
- SOR conditions after on-line cleaning should be always

compared (if feedstock has not been changed) with SOR conditions after mechanical cleaning or SOR conditions of the 1st startup.

- When on-line cleaning becomes more frequent (with the same feed and cracking conditions), it is time for mechanical cleaning.
- The author has noted that some fouling along tubes is so hardened that strong and insistent mechanical cleaning can locally damage the tube surface.
- TLE design with no anti-erosion devices at the inlet are preferred to avoid impingement and turbulence.
- TLE design with flushed tube-to-tubesheet joints (no welding step) are preferred to avoid impingement and turbulence.
- TLE design with tubes of larger diameter should be used when tube clogging is expected. **HP**

NOTES

These suggestions are given for reference only and are irrespective to any economic consideration and furnace conduction practices.

LITERATURE CITED

Complete literature cited available online at www.HydrocarbonProcessing.com



GIOVANNI MANENTI has more than 20 yr of experience in process and heat transfer design and R&D activities, and in engineering and pressure vessels manufacturing companies. He is focused on special shell-and-tube heat exchangers, such as process gas boilers for the syngas industry and transfer-line exchangers for steam cracking furnaces, and on heat transfer prototype equipment. Dr. Manenti earned a PhD in chemical engineering from Politecnico di Milano, Italy.

Bolting material bolts-up the exchanger design

Shell-and-tube heat exchangers use multiple girth flange joints based on their Tubular Exchangers Manufacturers Association (TEMA) type to assemble shell and tube sides. This permits their disassembly, inspection and cleaning.¹ Peripheral gaskets and fasteners play a key role in finalizing the geometry of any flange. Corrosive and environmental cracking services may dictate the requirements for directly exposed bolting materials to specific grades, per international standards, such as NACE MR0175/MR0103.²

This article details a case where the use of special service bolting material grade led to an excessively large external flange joint, resulting in heat exchanger overweight. It also describes the proposed solution by adjusting the extent of insulation on the exchanger, directly exposing the bolting material to atmosphere rather than the insulated sour service, which allowed the use of alternative higher strength bolting material grade.

Case description. This exchanger serves as a kettle-type chiller and propane-based

liquid refrigerant on the shell side, which extracts heat from tube-side, wet hydrogen sulfide (H_2S) (3,500 ppmv) hydrocarbon gas. Because of the upstream process, this complies with NACE MR0175. The main process and design parameters from the exchanger datasheet include:

- **TEMA type/size:**
 - TEMA type: AKU
 - Size: 2.15 m/2.92 m–6.1 m
- **Heat duty:** 8.3 MW
- **Design code:** ASME Sec VIII, Div. 2, Cl 1
- **Operating temperature:**
 - Shell side: 26°C/28°C
 - Tube side: 46°C/32°C
- **Design conditions:**
 - Shell side: 30 barg/150°C/(-) 21°C
 - Tube side: 90 barg/150°C/(-) 21°C
- **Shell and flange materials:**
 - Shell side: SA-516 Gr. 70N, SA-350 LF2 Cl 1
 - Tube side: SA-516 Gr. 70N (HIC), SA-350 LF2 Cl 1
- **Bolting material:** SA-320-L7M/SA-194-2HM
- **Insulation:**
 - Shell side: Cold conservation

- Tube side: Cold conservation.

Problem statement. The heat exchanger size and quantity are finalized in a front-end engineering design (FEED) package as an input document from the owner. Upon verifying the mechanical design—before issuing the datasheet in the material requisition in the detailed design phase—it was found that flange outside diameter (OD) with SA-320-L7M bolting material went beyond 4.5 m, with a weight of 63 metric t (tonnes), while the complete exchanger weight was approximately 350 metric t.

These dimensions and weights were unacceptable from plot space (the exchanger is installed in a module structure), transportation, maintenance, and even fabrication and cost perspectives.

The prime reason for this is the NACE bolting material grade SA-320 L7M used. ASME Section II limits its size to a maximum of 64 mm, and it has a lower allowable stress compared to L7 and L43 grades. Due to its lower strength and size, and to meet the root bolting area requirement, the quantity of studs had to be increased, leading to a higher bolt circle diameter (BCD) and larger flange OD, compounding the problem.

The FEED package states that the exchanger will be completely insulated to

TABLE 1. Table A.4 from NACE MR0175: Acceptable bolting materials in wet H_2S service

Bolts	Nuts
ASTM A193 grade B7M	ASTM A194 grades 2HM, 7M
ASTM A320 grade L7M	



FIG. 1. Proposed extent of insulation.

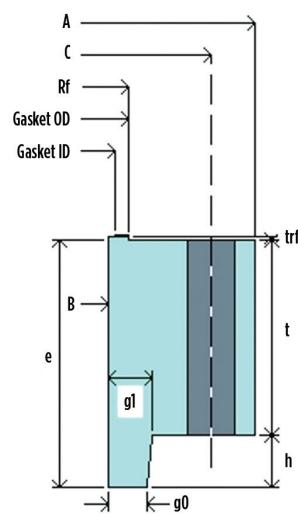


FIG. 2. Utilizing alternate bolting materials.

TABLE 2. Comparison of flange dimensions

Parameter	L7M	L7	L43
Flange ID [B], mm	2,150	2,150	2,150
Flange thickness [t], mm	640	550	370
Bolts quantity	104	84	44
Bolt diameter, mm	64	64	90
Bolt circle diameter [C], mm	4,420	3,570	2,535
Flange OD [A], mm	4,550	3,690	2,703
Flange weight, metric t	63	31	7

limit the heat gain from atmosphere with an ambient temperature of 52.7°C. Client specifications and NACE MR0175 limit the studs material grade to B7M and L7M, which are directly exposed to sour service environment or are in potential exposure. Refer to Table A.4 from NACE MR0175 (**TABLE 1**) for acceptable bolting materials in wet H₂S service.

Solution. The client was approached with the following recommended solution (**FIG. 1**) in two steps. The first step was adjusting the extent of insulation:

- Leaving the main girth flange joints un-insulated. This would allow the studs to be in direct exposure to atmosphere and avoid the potential exposure to sour service situation, as in the insulated case.
- The calculated heat gain of 26°C and 32°C from the surface temperature was 425 W/m² and 329 W/m², respectively, considering 52.7°C as an ambient temperature. Based on the proposed un-insulated surface area at the tube and shell

sides, the maximum heat gain at the tube side was 2,632 W; at 0.03% of the exchanger duty, this was insignificant. Since the exchanger is installed in a modular structure and contains enough obstructions from direct sunlight, no solar radiation impact was considered on un-insulated surfaces.

- The un-insulated flange joint will assist in early detection of toxic H₂S gas in case of flange leakage.

The second step utilized alternate bolting material (**FIG. 2**):^{3,4}

- Based on minimum design metal temperature (MDMT), the client's standard restricts the bolting grade to L7 for non-sour services. This stud has a higher allowable stress by 25% than L7M, but the size is still limited to 64 mm by ASME Section II.
- The use of L7 studs results in a flange OD of 3.7 m, which is again not a reasonable size. An acceptable recommended alternative was to use the L43 grade, which has the same strength as L7, but a higher sizing

limit to 100 mm. With this, the final flange OD is 2.7 m and the complete exchanger weight is 125 metric t.

This recommended solution will lead to an eventual estimated savings of more than \$1 MM for each exchanger.

TABLE 2 gives a comparison of flange dimensions designed per ASME Section VIII, Div. 2, Class 1 with SA-350 LF2 Cl. 1 materials for different bolting material grades for SA-320. **HP**

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Pressure instruments provide advanced connectivity

Endress+Hauser has released its new Cerabar and Deltabar pressure and differential pressure instruments (FIG. 1), with a Bluetooth interface for easier operation and improved efficiency in regulatory control, safety and other systems. Heartbeat Technology creates the data basis for predictive maintenance and allows the instruments' functionality to be verified without process interruption.

Endress+Hauser's new Cerabar and Deltabar pressure transmitters offer a user-friendly user interface. Intuitive operation is now provided via the SmartBlue app, which includes guided operating sequences for parameterization and commissioning of the pressure sensor, bridging distances of up to 50 ft. Measuring points that are difficult to reach or in hazardous areas are easy to maintain, even if they are only integrated into the process via a 4mA–20mA interface.

Plant personnel do not have to connect a cable, and real-time data from the pressure transmitter is easily available without the need for permits to open the housing, or for safety equipment to reach the instrument.

The Bluetooth connection has a special protocol that meets the increased safety requirements in industrial applications, and all connectivity is password protected. The Fraunhofer Institute AI-SEC tested the interface for its level of cy-

bersecurity protection and rated it "high" for protocol and algorithm.

The NAMUR roadmap "Process-Sensors 4.0" names three key criteria for digital process sensors: wireless communication, sensor diagnosis and the provision of information about the sensor and the process. The new Cerabar and Deltabar product lines meet these criteria, providing a solid foundation for implementing an IIoT strategy.

For example, Heartbeat Technology supports maintenance staff when verifying measuring points. This can be done via a Bluetooth connection and at the touch of a button with the SmartBlue app, which can be hosted on a smartphone or the Endress+Hauser SMT70 tablet, which is rated for use in hazardous areas. The verification can be carried out in less than 3 min without process interruption. A verification protocol, which provides detailed information about all tests, is generated automatically.

Continuous self-diagnostic functionality provides a coverage rate of more than 95%. With this information, it is possible to plan system revisions and maintenance work in advance to reduce downtime significantly and simplify the maintenance processes.

Heartbeat Technology provides users with the tools needed to optimize production through data-based insights into the process by providing transparency about the condition of the instruments and the process. It also detects irregularities in the process, for example deviations in the loop resistance, which in turn indicate a defective cable. Blocked impulse lines, e.g., due to crystallized medium, are detected by differential pressure transmitters. This type of data provides the basis for predictive maintenance.

Heartbeat Technology's diagnostic, monitoring and verification functionalities allow users to more efficiently interact with their instruments to improve process productivity. For example, predictive maintenance and better diagnostic information or in-situ health verification

result in less unscheduled downtime.

Guided operating sequences support plant personnel during the commissioning of measurement points and during SIL proof tests by showing technicians what to do, step by step. This prevents operating errors and systematic errors to improve safety. These tasks can also be completed more quickly because there is no need to consult a manual.

The new color display also provides safety at first glance. In the event of an error, it switches from green to red and thus provides a quick overview.

The new Cerabar and Deltabar instruments feature proven, reliable and robust sensor technology. New pressure measurement technology includes self-explanatory and efficient operating instructions to prevent systematic errors during instrument parameterization. These features maintain the high safety level of the system and at the same time reduce maintenance costs, during commissioning as well as maintenance.

Closer to the self-optimizing plant

With the release of aspenONE V12.1, AspenTech has embedded Industrial AI into its most widely adopted, industry-leading products and solutions, and empowered data scientists to collaborate with domain experts to enrich models. Now, even higher levels of profitability and sustainability can be achieved with new innovations that enable users to:

- Solve complex problems more effectively by tuning first principles models with AI
- Accelerate value with higher quality, accuracy and access to enterprise data
- Provide intuitive guidance to better support users
- Automate and simplify the creation and sustainment of models
- Reduce total cost of ownership
- Exchange data and models between domain experts and data scientists



FIG. 1. Endress+Hauser's new Cerabar and Deltabar pressure and differential pressure instruments.

- Accelerate the use of models for sustainability use cases.

New innovations in performance engineering, production and value chain optimization, asset performance management and Artificial Intelligence of Things (AIoT) transform how organizations work by embedding AI and decades of domain expertise into fit-for-purpose industrial applications. In aspenONE V12.1:

- Performance engineering embeds AI directly into process simulations to easily build operations-ready models calibrated with relevant plant data. Add AI-driven 3D conceptual layouts with the introduction of Aspen OptiPlant™ and Aspen OptiRouter™.
- Production and value chain optimization leverages deep learning and reduced order hybrid models to deliver more accurate, powerful and sustainable models that cover a broad range of operating conditions. In addition, the new Aspen Unscrambler™ and Aspen Process Pulse™ products use analytics, monitoring and optimization to improve process and product quality.
- Asset performance management brings new connectivity and performance for broader device and enterprise coverage, and more efficient alert management.
- Aspen AIoT Hub™ (Artificial Intelligence of Things) provides a fit-for-purpose, cloud-ready Industrial AI infrastructure to unlock significant value from data assets across the enterprise, while delivering actionable insights faster than ever before.

With aspenONE V12.1, users can accelerate their digitalization journey and leverage Industrial AI to increase margins, reduce costs and achieve safer, more sustainable operations.

Real-time visual monitoring of methane emissions

MIRICO has released MIRICO CLOUD, an online platform that enables real-time visualization of emissions data collected from its high-precision gas sensing instruments.

MIRICO CLOUD takes this data and

lets customers visualize the detection, localization and quantification of gas emissions across multiple oil and gas sites, all in one place. By producing results in real time, customers can act quickly to fix issues causing changes in emissions, enabling them to decrease or even eliminate downtime and reduce the risk of fines from environmental authorities.

To help customers react as quickly as possible, MIRICO CLOUD also provides notifications based on custom parameters, either via SMS or email. For example, to be alerted of new emissions above a certain size, or about existing known emissions that have started to grow.

The easy-to-use interface allows customers to see the layout of each of their sites, and overlay this with information such as path averages, location of detected emissions and quantification of any leaks. This information can all be viewed in real time with the ability to see historical data and track changes over time.

Through the customizable dashboard, customers can also view high-level, key information, such as average emissions over the last 24 hr, or see how emissions vary by asset type.

Uninterrupted power supply maximizes machine availability

As more power-sensitive devices are deployed in automated industrial processes, the need for reliable battery backup power is growing exponentially, yet serious challenges remain in the design of traditional uninterrupted power supplies (UPSs). Most UPSs are simply too large or heat-sensitive to be installed in control cabinets or to be integrated into machines, and virtually all lack the network communications required for remote diagnostics.

To address these challenges, Emerson has launched its SolaHD SDU AC-B UPS (**FIG. 2**), which combines a compact footprint with a wide operation temperature range and offers optional network communications supporting all major industrial protocols. Built rugged for harsh and hazardous locations, the SolaHD SDU AC-B supports organizations by bridging power failures during outages to allow for safe shutdowns of machinery, and by mitigating power quality issues that adversely affect critical loads, minimizing work interruptions, long restart cycles and the



FIG. 2. Emerson's SolaHD™ SDU AC-B UPS.

loss of data at the point of use.

Industrial engineers are facing increasing pressure to find additional space for components on DIN rails within control panels and enclosures, and in OEM machinery such as fabrication tools, robotics and CNC machines. The SolaHD™ SDU AC-B features a compact footprint, providing design flexibility without compromising protection to critical loads exposed to power aberrations. Measuring only 4.87 in. × 11.1 in. × 4.81 in. (h × w × d), it saves space while protecting against all types of power problems in critical applications that cannot afford downtime, including those requiring ODVA compliance.

Heat is the enemy of UPS batteries, especially in non-climate controlled environments, such as petrochemical plants, where elevated temperatures will dramatically shorten battery service life. The SolaHD SDU AC-B features a high heat, field replaceable battery rated from 32°F–122°F (0°C–50°C) that is thermally isolated from internal heat generating elements of the UPS. Combined with high-temperature grade components and an advanced battery management system, the SolaHD SDU AC-B adds value and long-term reliability in challenging environments.

As an option, the SolaHD SDU AC-B has an integrated communication port that supports both active and passive modules. Installing an active module is suitable for both general purpose and for high-end applications with large I/O data transfer, fast network cycles and synchronization demands communicating on either EtherNet/IP, Modbus, Profinet or EtherCAT network protocols. Installing a passive module enables control of two relays. Web monitoring is standard on the SolaHD SDU AC-B that remotely displays UPS status, alerts, SMS notification and a historical log. **HP**

An expanded version of Innovations can be found online at www.HydrocarbonProcessing.com.